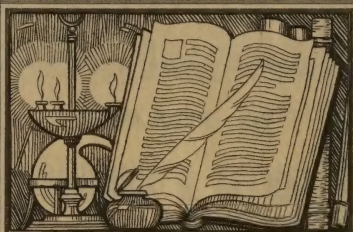




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# COLLOID CHEMISTRY

AN INTRODUCTION, WITH SOME  
PRACTICAL APPLICATIONS

BY

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ILLUSTRATED

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SECOND EDITION, REVISED AND ENLARGED



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## PREFACE TO SECOND EDITION

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The favorable reception accorded the first edition of this little book has led the author to enlarge and extend greatly this second edition, both in the theoretical and the technical sections, so that it may be used as an adjunct in teaching colloid chemistry, if not indeed as a text book. A large number of new practical applications have been introduced, and the effort has been made to develop the subject in a simple, coherent, and interesting manner, using, as far as possible, non-technical language and homely illustrations, so as to enable the reader's interest to aid memory.

The growing realization of the importance of colloid chemistry is evidenced by the fact, that, whereas the Decennial Index of Chemical Abstracts covering the years 1907-1916 contains only twelve columns of titles under Colloids, the 1922 Index alone contains five columns, and the 1923 Index contains four columns. These figures do not include many germane papers which are indexed under such headings as Adsorption, Diffusion, Coagulation, Gelatin, Gel, Sol, and a wide variety of physical, biological, and technical topics; but they do show that the colloidal zone is no longer "the world of neglected dimensions" as Wo. Ostwald once called it.

Matter in the colloidal state has unique properties which necessitate a revision of some of our preconceived notions; and this fact cannot be avoided by attempting to alter definitions and the established

meaning of language, or nullified by a Procrustean effort to fit all experimental data to existing theories.

To use a good old-fashioned term, we need *natural philosophers*, men whose view of the various fields of science is sufficiently broad and keen to enable them to see, understand, and correlate correctly apparently scattered facts in physics, chemistry, biology, technology, and related branches.

Science is not a sporting event. The true scientist's slogan is not "May the best man win," but rather "May the truth prevail."

Colloid chemistry comes not to destroy, but to fulfill. It does not destroy or even replace the known facts of chemistry, physics, and other sciences, but draws attention to certain aspects of Nature which have often been overlooked.

JEROME ALEXANDER

50 EAST 41ST ST.,  
N. Y. CITY,  
July 1, 1924

## PREFACE TO FIRST EDITION

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This little book is the result of an attempt to compress within a very limited space the most important general properties of colloids, and some of the practical applications of colloid chemistry. Its object will be accomplished if it is helpful in extending the sphere of interest in this fascinating twilight zone between physics and chemistry.

J. A.

NEW YORK,  
Nov. 1, 1918





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# COLLOID CHEMISTRY

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## CHAPTER 1

### INTRODUCTION

Although many facts and principles concerning colloids have from time immemorial been known and utilized empirically, the scientific foundation of modern colloid chemistry was laid by an Englishman, Thomas Graham, F.R.S., Master of the Mint. In two basic papers on this subject, the first entitled "Liquid Diffusion Applied to Analysis," read before the Royal Society of London, June 13, 1861, the second entitled "On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances," published in the *Proceedings of the Royal Society*, June 16, 1864, Graham pointed out the essential facts regarding colloids and the colloidal condition, and established much of the nomenclature in use at the present day. In the first of these papers Graham says: "The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to pos-

sess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina and other metallic peroxids of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of this class as colloids, and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as crystalloids. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary sense,



colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a pectous modification; and they often pass under the slightest influences from the first to the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. (H. Rose.) The colloidal is, in fact, a dynamical state of matter, the crystalloidal being the statical condition. The colloid possesses *Energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place

(for they always demand time as an element) may the characteristic protraction of chemico-organic changes also be referred. . . .

“It may perhaps be allowed to me to apply the convenient term dialysis to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper. . . .”

At the beginning of the second paper above referred to, Graham states: “The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal solutions.” From this it may be seen that Graham appreciated the fact that all the laws of crystalloidal solutions could not be applied to colloidal solutions. In the case of crystalloidal solutions the dissolved substance is present in a state of molecular subdivision, and, according to the ionization theory, is in many cases dissociated into ions. With colloidal solutions, on the other hand, we have a lesser degree of subdivision, and the particles in solution are larger and more cumbersome. As Graham remarked, “The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidity may not really be this composite character of the molecule.” This is to-day the idea generally accepted.

### Colloid Chemistry Defined

Colloid chemistry deals with the behavior and properties of matter in the colloidal condition, which,

as we now know, means a certain very fine state of subdivision. While there are no sharp limitations to the size of particles in colloidal dispersions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than a wave length of light, and extends downward well into dimensions which theory ascribes to the molecules of crystalloids. (See Table II, p. 27.)

### Suspension vs. Solution

With the aid of the ultramicroscope, which renders visible particles approaching in minuteness molecular dimensions, Zsigmondy has shown that there is no sharp line of demarcation between suspensions and colloidal solutions, but that with increasing fineness in the subdivision of the dissolved substance, there is a progressive change in the properties of the resulting fluids, the influence of gravity gradually yielding to that of the electric charge of particles, of surface tension and of other forms of energy. Thus in the case of metallic gold, subdivisions whose particles are  $1\ \mu$  and over act as real suspensions and deposit their gold, whereas much finer subdivisions ( $60\ \mu\mu$  and under) exhibit all the properties of metal hydrosols or colloidal solutions. In the ultramicroscope the coarser subdivisions show the well-known Brownian movement, which greatly increases as the particles become smaller, until at the present limit of ultramicroscopic visibility (about  $5\ \mu\mu$ ) it becomes enormous both in speed and amplitude.

On the other hand, there is no sharp distinction between colloidal and crystalloidal solutions, but as the particles in solution become smaller and smaller, the

optical heterogeneity decreases correspondingly, finally vanishing as molecular dimensions are approached.\* That even crystalloid solutions are not in a strict sense homogeneous, is indicated by an experiment of van Calcar and Lobry de Bruyn (*Rec. Trav. chim. Pays-Bas*, 1904, 23, 218), who caused the crystallization of a considerable part of saturated crystalloid solutions at the periphery of a rapidly rotating centrifuge.

\* In an article entitled "Pedetic Motion in Relation to Colloidal Solutions" published in *Chemical News*, 1892, Vol. 65, p. 90, William Ramsay, Ph.D., F.R.S. (afterward Sir William Ramsay), clearly expressed this view in the following words: "I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum*."

## CHAPTER 2

### MATERIAL UNITS AND THE FORCES DOMINATING THEM

Next to accurate observation and due allowance for all influential factors involved, perhaps nothing is more important in scientific matters than the mental separation of seasoned facts from the theories designed to systematize and explain them. For facts are hard, stubborn things that survive the theories whose downfall they may cause.

A theory must interminably run the gauntlet of the whole far-flung tribe of scientists, and may be stricken down after long years of apparent safety. Einstein's Theory of Relativity has been checked by astronomers and physicists in such diverse fields as the deflection of alpha particles shot out from radium, the deviation of starlight by the sun, and the precession of the axis of the orbit of the planet Mercury. How convenient it would be if a scientist, when confronted with facts that run counter to the very theories he has been taught to revere, could only say, as Ko-Ko remarked to Pooh-Bah:—"Come over here where the Lord High Treasurer can't hear us!"

### Divisibility of So-called Elements

Among the disconcerting discoveries of recent times may be mentioned those connected with radio-activity, which eventually led to the demonstration that electricity consists of discrete particles, and that our supposedly infrangible elements are complexes of positive and negative electrons, and that some of these



complexes are breaking up spontaneously and uncontrollably, while others may be shattered by the terrific impact of alpha particles moving at the rate of 10,000 miles or more per second.\*

Then the basic assumption of Dalton's atomic theory fell, when T. W. Richards, J. J. Thompson, Aston, Dempster, Harkins and others showed that with many of the elements, the atoms are not all alike, but have different atomic weights.

It is startling to learn, for example, that lithium consists of a mixture of atoms having atomic weights of 6 and 7, chlorine of atoms having atomic weights of 35 and 37, and that krypton has six *isotopes*, as they are called. In an address before the Chemical Society (London) Aston remarked:—"Though as a chemist I view with some dismay the possibility of eighteen different mercuric chlorides, as a physicist it is a great relief to find that nature employs at least approximately standard bricks in her operations of element building." And, to the endless disgust of small boys, Harkins has pointed out the possibility of 63 different kinds of calomel.

Some of our other new discoveries cast doubt upon what were heretofore accepted as facts. Thus the recognition of vitamins and certain salts as food essen-

\* To give an idea of the minuteness of an electron, Prof. R. A. Millikan states that if the entire population of Chicago, estimated at 2,500,000 people, were to begin to count the number of negative electrons passing as an electric current through an ordinary incandescent lamp in one second, and were to count continuously day and night at the rate of two per second, it would take them about 20,000 years to finish the count. In the highest vacuum we can produce, the number of residual molecules is so great that in each cubic inch there is a molecule for every inhabitant of the earth.

tials has necessitated the revision of conclusions drawn from some previous experiments on food values, which in some cases showed simply the minimum quantities of food needed to supply the necessary amount of vitamins or salts. The incompleteness of mere calorie-fat-protein-carbohydrate specifications is now well recognized.

### Chemical vs. Physical Forces

We make free use of the expressions "physical mixture" and "chemical compound" with the full confidence that we know exactly what we are talking about. But when we attempt to define these terms exactly, we appreciate the truth of Aristotle's remark that to frame an exact definition requires complete knowledge.

The difference between chemical and physical attraction is explained in many elementary text books by taking the example of iron filings and flowers of sulphur. From their physical mixture the iron may be separated magnetically or the sulphur dissolved out by carbon bisulphide; and the two ingredients may be separately identified in the microscope. If they are heated, however, the non-magnetic chemical compound  $\text{FeS}$  is formed, from which  $\text{CS}_2$  extracts no S. Furthermore, while Fe and S may be physically mixed in any desired proportions, in the chemical compound  $\text{FeS}$  they combine in the definite proportions of 56 parts by weight of Fe to 32 parts by weight of S, and any excess of S may be dissolved out by  $\text{CS}_2$ .

This fixes homogeneity and closeness of union in definite proportions by weight, as criteria of chemical combination.

But the transition between chemical and physical forces is not so sharp as our definitions demand; and it is in the transition zone that there appear the phenomena encountered in that extremely fine state of subdivision or dispersion known as the colloidal condition, where combination depends *not* upon the *total mass* involved, but upon the *total free or active surface*.

### The Sub-microscopic Structure of Matter

A whole series of complexities underlie even the smallest particle of matter visible in the most powerful microscope. Negative electrons, and protons or positive electrons are the only material units not at present *known* to be complex. While the number of steps in this series may vary in individual cases, in many instances the following degrees of aggregation may be definitely traced.

Material Unit	Order of Size*	Order of Complexity	Mode of Examination
Protons .....	$10^{-9} \mu\mu$	0?	Positive ray and particles from radium
Electrons.....	$2 \times 10^{-6} \mu\mu$	0?	Electric field, while floating on ultramicroscopic particles
Atoms.....	$0.1-2.0 \mu\mu$	1	X-ray spectrometer
Molecules.....	$0.5-5.0 \mu\mu$	2	X-ray spectrometer
Molecular Groups.....	$1-10 \mu\mu$	3	Diffusion and Ultramicroscope
Primary Colloidal Particles.....	$2-20 \mu\mu$	4	Diffusion and Ultramicroscope
Secondary Colloidal Particles.....	$5-100 \mu\mu$	5	Diffusion and Ultramicroscope
Microscopically Resolvable Particles.....	over $250 \mu\mu$	6	Microscope
Visible Particles.....	about $10 \mu$	7	Eye

\* Diameter.

Taking Shapleigh's estimate of the diameter of the galaxy of 300,000 light years = approximately  $2.5 \times 10^{21}$  cm., we see that in an exponential range of 37 \* we may pass from the smallest known material unit, the proton, to the outermost confines of the universe. This indicates the extent of the variations in real values represented by the  $p_H$  exponential figures so often used to express the effective acidity or alkalinity of colloidal solutions. When using Sörensen's convenient  $p_H$  symbolism we must remember that it is an inverse exponential function.

### Hydrogen Ion Concentration

The expression  $p_H$  demands some explanation. It is a convenient way to express the reaction of any fluid, but is dangerous because it does not do this directly; for it is an inverse logarithmic function, deprived of its minus sign, as will be seen directly.

Pure water dissociates slightly according to the equation



the reaction being reversible. It has been found that at 22° C. the concentration of hydrogen ions in pure

water equals  $\frac{1}{10,000,000}$  moles per liter, a fact usually

expressed by the symbolism  $C_{H^+}$  (concentration of hydrogen ions) equals  $10^{-7}$  moles per liter. Since for each  $H^+$  ion in water there is an  $OH^-$  ion,  $C_{OH^-} = 10^{-7}$  under the same conditions.

\* That is the proton has a diameter of the order of  $10^{-16}$  cm. and the galaxy a diameter of the order of  $10^{21}$  cm., the exponential spread being 37.

Now, for convenience, Sørensen proposed to disregard the minus sign, and to use simply the numerical value of the exponent of 10 to express the reaction represented by the corresponding  $C_{H^+}$ . The following table\* will make this clear:

	Degree of normality	$C_{H^+}$	Equivalent $p_H$ value
HCl	1.0	$8.0 \times 10^{-1}$	0.10
	0.1	$8.4 \times 10^{-2}$	1.07
	0.01	$9.5 \times 10^{-3}$	2.02
	0.001	$9.7 \times 10^{-4}$	3.01
	0.0001	$9.8 \times 10^{-5}$	4.01
Acetic acid	1.0	$4.3 \times 10^{-3}$	2.37
	0.1	$1.6 \times 10^{-3}$	2.87
	0.01	$4.3 \times 10^{-4}$	3.37
	0.001	$1.6 \times 10^{-4}$	3.87
Caustic soda	1.0	$0.90 \times 10^{-14}$	14.05
	0.1	$0.86 \times 10^{-13}$	13.07
	0.01	$0.76 \times 10^{-12}$	12.12
	0.001	$0.74 \times 10^{-11}$	11.13

This table shows that the lower the  $p_H$  value, the greater the *effective reaction* of acidity, which is something quite different from the *total* acidity. Thus equal volumes of normal hydrochloric acid and of normal acetic acid will neutralize equivalent volumes of normal alkali, but the normal acetic acid has a much lower degree of acidity or hydrogen ion concentration, and therefore a higher  $p_H$  value.

Not only does the  $p_H$  value run *opposite* the H ion concentration, but the variations are exponential or logarithmic, not arithmetical. The step between  $p_H$  5 and  $p_H$  6 is vastly less than the step between  $p_H$  5 and  $p_H$  4, as may be seen from the following table:

\* "Die Wasserstoffionen Concentration," by Prof. Lenor Michaelis.



pH value	Number of times H (or OH) ion concentration exceeds that of pure water	
1	1,000,000	
2	100,000	
3	10,000	
4	1,000	
5	100	acid side
6	10	
7	0	pure water—————
8	10	
9	100	
10	1,000	alkaline side
11	10,000	
12	100,000	
13	1,000,000	

### Homogeneity and Heterogeneity—Phases

Lewis and Randall ("Thermodynamics," p. 9) describe a *homogeneous system* as one in which there are no apparent surfaces of discontinuity; and a *heterogeneous system* as one consisting of two or more distinct homogeneous regions or *phases*, which appear to be separated from each other by surfaces of discontinuity. The celebrated Phase Rule of J. Willard Gibbs [Trans. Conn. Acad. Sci., 3, 228 (1876)] is that the number of degrees of freedom ( $F$ ) of a system as a whole (in other words the number of independent variables upon which it depends) equals the number of variables essential to determine the state of the individual phases, minus the sum of the phases outside the first.

Thus in a system of  $n$  phases whose individual states are controlled by  $x$  variables,

$$F = x - (n - 1) = x - n + 1$$

But as Zsigmondy pointed out (Colloids and the

Ultramicroscope, p. 3) and as the above table showing the serial complexity of matter indicates, the practical distinction between homogeneity and heterogeneity depends entirely upon the refinement of our means of observation. In many cases we assume phases to be homogeneous to simplify our calculations; but when a substance is finely subdivided or dispersed, the influence of specific surface (exterior or rind surface) becomes an important factor, the phases neglected or submerged for our convenience urgently demand consideration, and the number  $n$  in Gibbs' equation must be increased.

### Interfacial Anomalies

In all free surfaces the exterior molecules occupy a position quite different from the interior molecules, which are on all sides surrounded by their own kind. Part of the attractive forces of the surface molecules are directed inward, part toward adjacent surface molecules (thus forming a surface skin), and a residual unsatisfied portion outward. This residual affinity may be demonstrated by cleaving a piece of mica (muscovite) and instantly putting the new surfaces together. They exhibit considerable cohesion, although this represents but a fraction of the original attractive force, and is soon lost by further adsorption of atmospheric constituents. A fresh iron surface absorbs atmospheric constituents so quickly that, although a piece of cast iron broken under mercury is amalgamated at its new surfaces, the same iron if broken above the mercury and instantly dropped in, is not amalgamated at all. (P. W. Bridgman.)

### Residual Affinities

If the attractive forces existing between atoms were entirely balanced or satisfied by their chemical combination, then every chemical compound would behave as a perfect gas so far as concerns the factor  $a$  in the equation of van der Waals. But in all chemical compounds exist residual attractions or stray fields of force which exert a controlling influence on what are ordinarily termed the physical properties of the compound—its state (gaseous, liquid or solid), its cohesion, solubility, boiling point, conductivity for heat and electricity, dielectric constant, etc. This residual attraction is responsible for the phenomena we call adhesion and adsorption, and its range of effective action (of the order of  $10^{-8}$  cm.) is much less than the diameter of a molecule.

Langmuir says that molecules usually orient themselves in definite ways in the surface layer, since they are held there by forces acting between the surface and particular atoms or atomic groups in the adsorbed molecule. This accounts for the influence of chemical composition on adsorption commented on by Bechhold and others. Harkins (J. Am. Chem. Soc. 1920, 42, 706) points out that in organic compounds this orientation depends upon the dissymmetry of the molecule. "An entirely symmetrical molecule (or atom in the case of monatomic liquids) would not orient at all, but such a molecule or atom does not exist. Molecules as symmetrical as those of the short chain saturated paraffins, carbon tetrachloride, etc., would not be expected to show such evidence of orientation as those molecules which may be considered as heavily loaded, from the standpoint of the stray

electro-magnetic field, at one end of the molecule and very light, in the same sense, at the other."

### A Simple Principle Underlying the Colloidal State

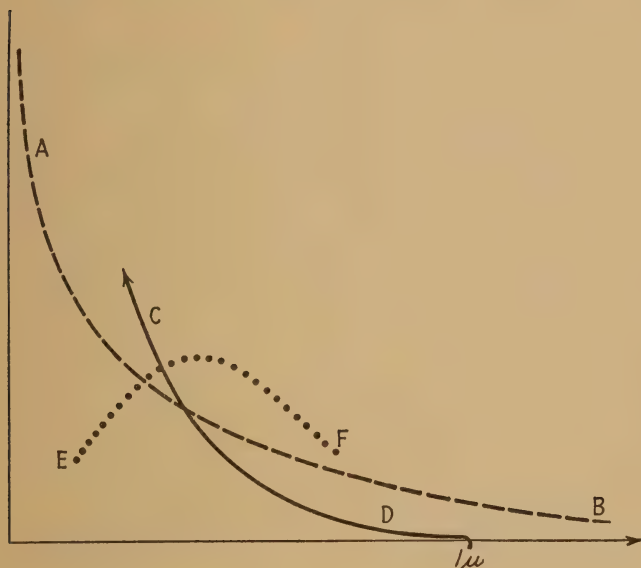
The anomalous properties exhibited by matter in colloidal dispersion, as we follow it beyond the limit of microscopic resolvability to molecular dispersion, may be understood by considering two properties—(1) *specific surface* and (2) *kinetic activity*.

Specific surface (exterior or rind surface per gram) will vary considerably with the actual shape of the particles. If we assume an average spherical shape and plot specific surface against particle size, we obtain an hyperbola. For with infinitely large particles the free surface per gram approaches zero, and with infinitely small particles the free surface per gram approaches infinity; and the areas of spheres vary inversely as the squares of their radii. Therefore the curve is asymptotic to both axes and varies as  $d^2$ ; that is, it is hyperbolic.

The mean velocity of translation \* of particles is likewise subject to great variations; chemical nature, physical structure, viscosity of the dispersing medium, temperature; incidental ions, solutes, or impurities, all exercise their effects. But with the same substance, under the same conditions, the kinetic motion, beginning as the well-known Brownian motion at the limit of microscopic resolvability, increases at first slowly and then with gradually accelerating rapidity as subdivision proceeds; so that the curve of kinetic motion, plotted for convenience of comparison on the same axes as that

\* There is a kinetic motion of revolution as well as of translation, the observed translatory kinetic motion being the difference.

of specific surface, soon rises rather abruptly, and cuts the latter (see Fig. 1).



Increasing particle size

AB = free surface per gram; CD = kinetic motion curve; EF = rise and fall of colloidal characteristics.

Fig. 1.—Relation between kinetic activity and specific surface.

### The Zone of Maximum Colloidal

In following the gradual dispersion of a substance from gross visible particles all the way down to true molecular subdivision, it is obvious that in the colloidal zone there is a transition from a state where the kinetic activity is *small* as compared to the specific surface to a state where the kinetic activity is *large* as compared to the specific surface. In the heart of the colloidal zone there is usually observable an indefinite portion



of the curve which has been termed the *zone of maximum colloidal* (J. Alexander, J. Am. Chem. Soc. 43, 434 (1920), wherein colloidal properties, such as viscosity, are most marked.

The zone of maximum colloidal appears in a wide variety of substances—in steel (J. Alexander), in duralumin (Merica, Waltenberg & Scott), in dyeing (R. Auerbach). In his H. M. Howe Lecture (before the Am. Inst. Min. & Met. Engr. 1924) Prof. Albert Sauveur stated facts which disclose its existence in heated steel, which showed maximum strength over a certain temperature range. On adding water to acetone solutions of nitrocellulose, F. Sproxton (3d Report on Colloids, etc., Brit. Assoc. Adv. Science, 1920) found that the viscosity rose to a maximum and then fell. Sulfur at 150° has a viscosity of 8; at about 200° it rises to over 50,000, and at 400° it drops to 150. Viscose in ageing passes through a maximum of viscosity.

We may therefore *pass upward* into the colloidal state as molecules *aggregate or become larger*, or pass *downward* into the colloidal state as coarse particles are *more finely ground or dispersed*. Thus Martin H. Fischer showed that in taking sodium salts of the fatty acids beginning with sodium formate and passing through the acetate, propionate, etc., up to the stearate and oleate, we find that the water holding capacities of the salts increases steadily.\* His results may be tabulated as follows:

\* L. Lascary [Koll. Z., 34, 73 (1924)] found that the effect of sodium soaps on surface tension *increases* with molecular weight to sodium myristate, above which it *decreases*.

No. of  
Carbon  
Atoms

1...	Sodium formate....	molecular dispersion							
2...	" acetate....	"	"	"					
3...	" propionate..	"	"	"					
4...	" butyrate....	"	"	"					
5...	" valerate....	"	"	"					
6...	" caproate....	shows signs of holding water							
8...	" caprylate ...	1 mol. gives a jelly with	250 c.c. of water						
10...	" caprate....	1 " " " " "	500 c.c.						
12...	" laurate....	1 " " " " "	4,000 c.c.						
14...	" myristate...	1 " " " " "	12,000 c.c.						
16...	" palmitate...	1 " " " " "	20,000 c.c.						
17...	" margarate ..	1 " " " " "	24,000 c.c.						
18...	" stearate....	1 " " " " "	27,000 c.c.						
20...	" arachnate...	1 " " " " "	37,000 c.c.						

On the other hand, Victor Lehner reduced silica to colloidal solution by continued grinding; and colloidal gold may be produced by the Bredig or the Svedberg method of electrical spattering, as well as by the Faraday-Zsigmondy method of reducing gold chloride.

The above facts justify Svedberg's classification of methods for the formation of colloids into (a) *aggregation methods*, (b) *dispersion methods*.

### The Relation of Colloidal to Other Forces

Mendeléef in his suggestive paper, entitled "A Chemical Conception of the Ether," intimated that gravitation might be explained on the basis of etherial impact acting from all sides; for from this assumption the Newtonian laws of gravitation may be easily developed. This is evident from the following considerations:

Assuming that the ether is a subtle gas whose particles move with approximately the speed of light, and that mass represents the ability of a substance to reflect

the motion of ether particles, then any body, if alone in the universe, would be struck equally on all sides by the ether particles and if at rest would remain at rest, but if in motion would tend to maintain its rate of motion. This is *Newton's first law*; but it is obvious that if the motion of the body is large as compared with the motion of ether particles, then the moving body will appreciably increase in mass; for it will anticipate the blows of ether particles coming from the direction of its motion, and receive a diminished impact from those coming from the opposite direction (*relativity effect*).

As soon as we introduce a second body into our calculation, then each body *shadows* the other *in proportion to its mass* or ether-stopping capacity. This means an excess of ether pressure on the unshadowed side, so that the bodies attract each other directly as their masses. But since the areas of spheres vary inversely as the squares of their radii, it is obvious that a body removed to twice the distance will have only  $\frac{1}{4}$  the shadowing effect; at three times the distance only  $\frac{1}{9}$  the shadowing effect, etc. That is, the attraction between the bodies *varies directly as their respective masses and inversely as the square of the distance between them* (*Newton's second law*).

E. Cunningham ("Relativity and the Electron Theory") has shown that a material ether is not inconsistent with relativity, and the objective view of gravitation is much more appealing than recourse to "fields of force" without a material substratum, although, as Herbert Spencer pointed out, explanations of this kind simply transfer the enigma of Nature one step further back.

M. Le Sage in 1784 had expounded the same theory of gravitation, and Prof. S. P. Langley (inventor of the airplane) had a translation of Le Sage's work published by the Smithsonian Institution. It is possible that the nature of chemical attraction may be explained as a gravitational force modified because the reacting units are so close together that their size, shape and internal structure become material factors. We seem to be working toward the view maintained by Faraday and no doubt by many others, that there is one ultimate kind of force.

P. E. Wells (J. Wash. Acad. Sci. 1919, 9, 361) suggests the following classification of forces:

1. *Electronic Forces*—Maintain positive nucleus, and negative or valence electrons in equilibrium as a single system.

2. *Atomic Forces*—Maintain two or more atoms in equilibrium as a single system.

3. *Molecular Forces*—Maintain two or more molecules in equilibrium as a single system.

4. *Molar Forces*—Maintain two or more masses in equilibrium as a single system.

Electronic forces are thus responsible for atoms; atomic forces, for their chemical combination into molecules; molecular forces, for most physico-chemical and colloidal phenomena; and molar forces, for ordinary physical and astronomical phenomena. "Each group of forces," says Wells, "may be regarded as the residual fields of force remaining unsaturated in the smaller systems constituting the components of the system under consideration. . . . Molecular systems have lost so much of their discreteness that combinations of molecules do not follow the laws of definite

and multiple proportions. In such phenomena as molecular association and surface structure, the discreteness of atomic constitution begins to give place to statistical continuity. Moreover, in these phenomena the force are relatively so weak that molecules are not usually regarded as permanently grouped together."

Thus adsorption, molecular association, and condensation would be considered as molecular phenomena; and while polymerization may start that way, in it atomic forces predominate.

In reading over the numerous practical applications of colloid chemistry we will later consider, it must be remembered, then, that most of the reactions lack that preciseness indicated by the present meaning of the term "chemical compound." Slight deviations from previous conditions may involve a material difference in results, and until we understand and can give proper weight to all the underlying factors, many of our successful methods will remain "cooking recipes." Colloid chemical research is letting in a flood of light upon many reactions not amenable to the ordinary stoichiometric laws of chemistry, though in some cases they may closely approach these laws.

### Solution vs. Colloidal Solution

When the attraction of the molecules of a liquid for those of a solid exceeds the attraction of the molecules of the solid for each other, then the solid is dissolved or peptized by the liquid. If the dispersion is profound enough, the solute may go into true or crystalloidal solution, but if the molecules of the solute cling to each other to a considerable extent, they may form



groups of colloidal dimensions, and there results a colloidal solution.\*

The degree of dispersion in which a substance exists in a solution naturally affects its kinetic activity, its speed of diffusion, and even its ability to diffuse. Thus sodium stearate is not a good protector nor even a good detergent until it is dissolved in sufficiently heated water; and in tanning and dyeing the degree of dispersion governs fixation capacity and speed. In the case of a kinetically balanced equilibrium, as with blood sugar, difference in diffusion speed may raise or lower the percentage of dextrose in the blood.

An interesting case is the action of selenium oxychloride on barium sulphate. As Lehner discovered, this remarkable solvent, which dissolves such diverse substances as rubber and gelatin, converts the highly insoluble barium sulphate into a colloidal jelly. Molecular groups having a great tendency to dissolve are sometimes able to drag into solution with them attached groups which would otherwise be insoluble. Thus many aniline dyes and even oils are sulphonated in order to make them "soluble" in water, where they usually form colloidal dispersions.

### The Nature of Adhesion

Our principal adhesives, such as gums and glues, are substances which because of the makeup of their molecules possess powerful residual fields of force and are therefore capable of attaching themselves to other substances possessing residual fields of the opposite charge. They must besides have sufficient residual

\* Indeed, with most solutes and with most solvents, too, there is a certain degree of molecular association, as it is called. Liquid water is mainly dihydrol ( $\text{H}_2\text{O}$ )<sub>2</sub>.

force to cling powerfully to adjacent molecules of their own kind. Thomas Graham long ago remarked that colloids as a rule adhere better to each other than to crystalloids. One reason probably is that colloids possess a plurality of residual fields which may have different charges at different points. They are also highly polar.

Adhesion is purely a matter of surfaces. Glue will stick paper to wood, but not to paraffin or to wood having a paraffined surface. It is true that glue will hold paper to paraffin or to bright tin until the adhesive dries; then the powerful attraction of the glue particles for each other as they are dehydrated breaks the weak bond between the glue and the paraffin or metal, although it is unable to break the bond with the paper to which the other face of the glue layer clings tightly.

### Surface Forces in Grinding or Pulverizing

It is not an easy or inexpensive operation to dry grind most substances below 200 mesh. As subdivision proceeds, the total free surface increases enormously, and apart from the inherent difficulty of breaking up a very fine particle, the tendency of the fragments to reunite or "cake up" begins to assert itself. The finer the particles the greater this tendency, and it is increased by pressure. It is to a large measure overcome by wet grinding, because the adsorption of fluid or solutes at the new surfaces tends to prevent their reunion.

### The " Colloid " Mill

This is essentially a high speed disintegrator arranged for wet grinding, and the patents of Block, Plauson and China relate chiefly to mechanical details. A readily absorbable substance (a deflocculator or protective colloid) is added to the liquid in the mill, and stabilizes the colloidal dispersion as it is formed.

Block's machine, has a very high speed rotor eccentrically placed in a casing of circular cross section. The high peripheral speed of the rotor forces the material to be pulverized, practically under pressure, into the space between the rotor and the casing, where most of the atomization occurs, the material to a large extent grinding against itself.

The mill can be used to make emulsions, and colloidal solutions of cellulose and highly concentrated colloidal mercury have been made with it. It is said to be used in the soap industry for speeding up saponification; in the dairy industry for homogenizing milk and cream; in producing colors, inks, rubber goods, etc. No doubt it will produce many desirable results, but since high speed takes power and means wear, the commercial advantages of the mill remain to be demonstrated. (See e.g. 8th Report on Progress of Applied Chemistry, Soc. Chem. Ind., 1923, page 340).

## CHAPTER 3

### CLASSIFICATION OF COLLOIDS

The broadest classification of colloids is that of Wolfgang Ostwald (*Koll. Zeitschr.*, Vol. 1, page 291), who grouped them according to the physical state (gaseous, liquid or solid) of the subdivided substance (dispersed phase), and of the medium in which the particles of the subdivided substance are distributed (dispersion medium).<sup>\*</sup> Table I below shows the nine resulting groups and gives some instances of each.

Ostwald's classification, however, is more theoretical

TABLE I

Dispersed phase.	Dispersion medium.	Example.
Gas.....	Gas.....	No example, since gases are miscible in all proportions.
Gas.....	Liquid.....	Fine foam, gas in beer.
Gas.....	Solid.....	Gaseous inclusions in minerals (meerschäum, pumice), hydrogen in iron, oxygen in silver.
Liquid.....	Gas.....	Atmospheric fog, clouds, gases at critical state. <sup>†</sup>
Liquid.....	Liquid.....	Emulsions of oil in water, cream, colloidal water in chloroform.
Liquid.....	Solid.....	Mercury in ointments, water in paraffin wax, liquid inclusions in minerals.
Solid.....	Gas.....	Cosmic dust, smoke, condensing vapors (ammonium chlorid).
Solid.....	Liquid.....	Colloidal gold, colloidal sodium chlorid, colloidal ice in chloroform.
Solid.....	Solid.....	Solid solutions, colloidal gold in ruby glass, coloring matter in gems.

<sup>\*</sup> G. Bredig proposed to call colloids "microheterogeneous systems." W. Ostwald called them "dispersed heterogeneous systems," which expression was contracted by P. P. von Weimarn into the term "dispersoids."

<sup>†</sup> A. Einstein, "Turbidity near the Critical State," *Ann. Phys.*, **33**, 1275 (1910).

TABLE II

Wave lengths of Light.	S u s p e n s i o n s		Microscopic Field.
	Colloidal Solutions		
	Reversible Hydrosols.	Irreversible Hydrosols.	
1 $\mu$			
0.1 $\mu$			Gold Suspension C
50 $\mu\mu$	Lea's Colloidal Silver Colloidal Indigo Paris blue sol. Gold Some Dyestuff Solutions Glycogen Solution Various Albumen Solutions	Colloidal Sulphids Many Colloidal Oxides Purple of Cassius	Colloidal Metals Bredig's Colloidal gold Au 101 Au 92 Au 73a Gold solutions with microscopic particles
20 $\mu\mu$			
5 $\mu\mu$	Soluble Starch? "Crystallized" Albumen? Crystalloid Solutions and Mixtures of Gases		
0.1 $\mu\mu$	Dextrin Dyestuffs Molybdic Acid		Ultramicroscopic Field.

### *Classification of Colloidal Solutions*

according to the size of the particles contained in them and  
according to their behavior upon desiccation.





than practical, for the properties of colloids are dependent mainly upon the specific nature of the dispersed substance and its degree of subdivision. Following Hardy, Zsigmondy divided colloids into two classes, the *reversible* and *irreversible*; the former redissolve after desiccation at ordinary temperatures, whereas the latter do not.

Table II, taken from Zsigmondy,\* illustrates this classification, and shows how colloids having the same particle size or degree of subdivision may nevertheless act quite differently because of specific differences in the nature of the dispersed substances.

With the reversible colloids (gelatin, gum arabic, albumen), there is a more intimate union between the two phases; in fact it is probable that with them we have really a mixture of (1) a dispersed phase of water subdivided in the solid, with (2) a dispersing phase of the solid finely subdivided in water. The reversible colloids are therefore called *emulsoids* and the irreversible colloids *suspensoids*. Colloids of the reversible type are also said to be *hydrophile* or *lyophile*, while the irreversible colloids are *hydrophobe* or *lyophobe*.†

No sharp line is to be drawn, however, for besides intermediate or transition cases between the two classes, there may be recognized two groups of irreversible colloids, roughly defined by their behavior upon concentration:

*First:* The *completely irreversible*, which coagulate while still quite dilute and separate sharply from the solvent with the formation of a pulverulent precipitate rather than a gel (i.e., pure colloidal metals). Chem-

\* "Colloids and the Ultramicroscope," J. Wiley & Son, Inc. (Translation by J. Alexander.)

† Hydrophile = water-loving; hydrophobe = water-hating. Lyophile = solution-loving; lyophobe = solution-hating.

ical or electrical energy is needed to bring them back again into colloidal solution.

*Second:* The *incompletely reversible* which, when quite concentrated, form a gel that may be easily redissolved or *peptisized* by comparatively small amounts of reagents, unless the evaporation has proceeded too far (i.e., colloidal stannic acid).

## CHAPTER 4

### CONSEQUENCES OF SUBDIVISION

As the subdivision of a substance proceeds, the area of its effective surface increases enormously, as may be seen from the following Table III adapted from Ostwald. Consequently surface forces, such as adsorption, capillarity and surface tension, become enormously magnified and of primary importance. Furthermore, the so-called radius of molecular attraction ( $\rho = 50 \mu\mu$ ) is well within the colloidal field, so that the specific attractive forces of the particles also enter as a controlling factor. In fact, before substances can unite chemically their particles must be first brought into proper subdivision and proximity,\* by solution, fusion, ionization or even by mere pressure, as was demonstrated by W. Spring, who caused fine dry powders to combine chemically by high pressure. If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or nonstoichiometric proportions, under the influence of more or less modified chemical forces. The combination of arsenious acid and ferric oxid which Bunsen regarded as a

\* It is a striking fact that absolutely dry sodium is not attacked by absolutely dry chlorin. M. Raffo and A. Pieroni observed that colloidal sulphur reduced silver salts energetically, whereas even fine precipitated sulphur did not form silver sulphide in the cold, and did so only partially upon boiling.

TABLE III. RESULT OF PROGRESSIVE DECIMAL SUBDIVISION OF A CUBE

Length of edge.	Number of cubes.	Total surface.
1 cm.	1	6 sq. cm. = 0.93 sq. in.
1 mm.	1,000	60 sq. cm. = 9.3 sq. in.
0.1 mm.	1,000,000	600 sq. cm. = 93 sq. in.
0.01 mm.	1,000,000,000	6000 sq. cm. = 6.46 sq. ft.
1 $\mu$	1,000,000,000,000	6 sq. m. = 64.58 sq. ft.
0.1 $\mu$	1,000,000,000,000,000	60 sq. m. = 645.83 sq. ft.
0.01 $\mu$	1,000,000,000,000,000,000	600 sq. m. = 6458.33 sq. ft.
1 $\mu\mu$	1,000,000,000,000,000,000,000	6000 sq. m. = 1.48 acres
0.1 $\mu\mu$	1,000,000,000,000,000,000,000,000	6 hectares = 14.83 acres
0.01 $\mu\mu$	1,000,000,000,000,000,000,000,000,000	60 hectares = 148.26 acres
*0.001 $\mu\mu$	1,000,000,000,000,000,000,000,000,000,000	6 sq. kilometers = 1482.6 acres
		= $2\frac{1}{3}$ sq. miles

\* These subatomic dimensions are 1000 times larger than the theoretical size of electrons

$$1 \mu = \frac{1}{1,000} \text{ mm.}; \quad 1 \mu\mu = \frac{1}{1,000} \mu.$$



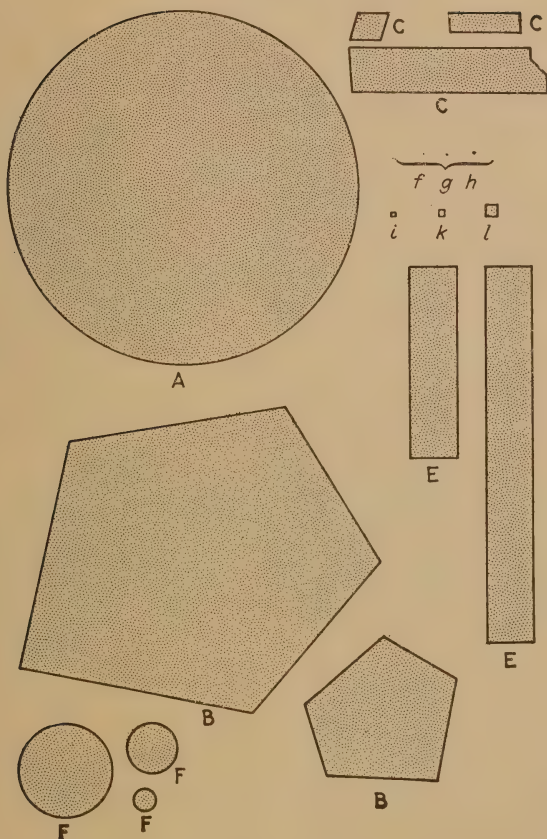
basic ferric arsenite,  $4 \text{ Fe}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $5 \text{ H}_2\text{O}$ , has been shown by Biltz and Behre to be an adsorption compound; and Zsigmondy proved "purple of Cassius" to be an adsorption compound of colloidal gold and colloidal stannic acid by actually synthesizing it by mixing the two separate colloidal solutions. Zsigmondy's proof has been further confirmed by A. Huber (*Physikal. Zeit.* (1924), 25, 45) who examined the purple of Cassius with the X-ray spectrometer and found that none of the gold is in chemical combination.

The effect of increasing subdivision upon the particles in colloidal solutions is illustrated in Table IV, adapted from Zsigmondy. Tables V and VI were prepared by Zsigmondy to illustrate visually the relation of the sizes of colloidal particles to well-known microscopic objects on the one hand and to the theoretical sizes of molecules on the other.

TABLE IV

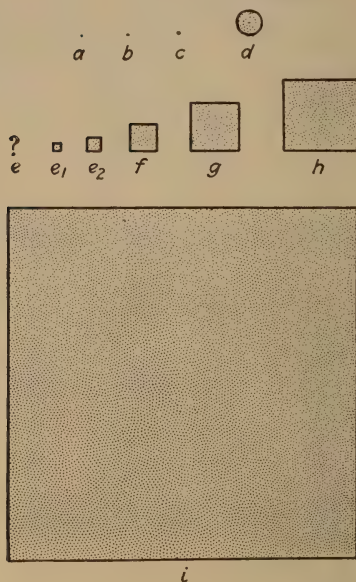
0.1 $\mu$	1 $\mu$	10 $\mu$	100 $\mu$	1 $\mu$	10 $\mu$	100 $\mu$	1 mm.
ULTRAMICROSCOPIC FIELD				MICROSCOPIC FIELD			
Particles visible but not resolvable Quartz no longer settles				Particles visible and resolvable Quartz settles			
Oil emulsion forms no cream layer				Oil emulsion forms a cream layer			
Particles pass through filter paper				Particles retained by filter paper			
Particles move very quickly				Brownian Movement not visible			
Crystalloid : Colloidal Dispersions : Dispersions				Suspensions			
"Cloudy solutions"							

TABLE V  
 LINEAR MAGNIFICATION 1:10,000



- A.** Human blood corpuscles (diameter  $7.5 \mu$ , thickness  $1.6 \mu$ ).  
**B.** Fragment of rice starch granule (according to v. Höhnelt)  $3-8 \mu$ .  
**C.** Particles in a kaolin suspension.  
**E.** Anthrax bacillus (length  $4-15 \mu$ , width about  $1 \mu$ ).  
**F.** Cocci (diameter about  $0.5-1 \mu$ , rarely  $2 \mu$ ).  
*f, g, h.* Particles of colloidal gold solutions  $\text{Au}_{73a}$ ,  $\text{Au}_{92}$ ,  $\text{Au}_{97}$  ( $0.006-0.015 \mu$ ).  
*i, k, l.* Particles from settled gold suspensions ( $0.075-0.2 \mu$ ).

TABLE VI  
 LINEAR MAGNIFICATION 1: 1,000,000



a-d. — *Hypothetical Molecular Dimensions*

- a. Hydrogen molecule — dia.  $0.1 \mu\mu$ .
- b. Alcohol molecule — dia.  $0.5 \mu\mu$ .
- c. Chloroform molecule — dia.  $0.8 \mu\mu$ .
- d. Molecule of soluble starch — dia. about  $5 \mu\mu$ .

e-h. — *Gold Particles in Colloidal Gold Solutions*

- e. Gold particle in  $\text{Au}_{16}$  (too small to determine).
- e<sub>1</sub>. " " " " , about  $1.7 \mu\mu$ .
- e<sub>2</sub>. " " " " , "  $3.0 \mu\mu$ .
- f. " " "  $\text{Au}_{720}$ , "  $6 \mu\mu$ .
- g. " " "  $\text{Au}_{92}$ , "  $10 \mu\mu$ .
- h. " " "  $\text{Au}_{97}$ , "  $15 \mu\mu$ .
- i. Gold particle in settled gold suspension.

## CHAPTER 5

### THE ULTRAMICROSCOPE

As this instrument revolutionized colloid research, a brief description of it is essential.

It is a matter of every-day experience that the unseen motes and dust particles in the air become visible in a beam of bright light, especially against a dark ground, and in this simple fact lies the principle of the ultramicroscope.

Faraday and later Tyndall made use of a convergent beam of light to demonstrate the optical inhomogeneity of solutions; for in fluids not optically clear, the path of the beam becomes more or less distinctly visible, because of the light scattered by the particles present. In this manner can be recognized much smaller quantities of matter than by spectrum analysis—in fact less than  $10^{-8}$  mg. (1/10,000,000) of metallic gold can thus be detected with the naked eye.

Prof. Richard Zsigmondy while experimenting with colloidal solutions conceived the idea of examining this light cone microscopically. His preliminary experiments having demonstrated that he could thus see the individual particles in various hydrosols, he sought the assistance of Dr. H. Siedentopf, scientific director of the Zeiss factory, in Jena, where was produced the first efficient ultramicroscope.

The ultramicroscope consists essentially of a compound microscope arranged for examining in a dark field an intense convergent beam of light cast within or upon the substance under examination. The light



seen by the eye represents, therefore, the light diffracted, scattered or reflected upward by the substance or by particles within it.

If within a thin beam of light from a projection lantern we scatter successively powders of different substances in various degrees of fineness (mica ground to pass 60, 100 and 160 mesh; lampblack; powdered oxid of zinc; flake and powdered graphite), some of them will produce only a homogeneous illumination of the beam in which no isolated particles can be seen, whereas with others, the individual particles are distinctly visible.

Passing the beam through a beaker of distilled water, nothing can be seen; but upon the addition of a few drops of colloidal gold solution, which appears quite clear to transmitted light, the path of the beam through the fluid immediately becomes visible. This Tyndall effect,\* as it is called, might be considered a criterion of colloidal solution were it not that very minute traces of colloidal impurities can produce it and it is often exhibited by solutions generally regarded as crystalloidal—those of many dyestuffs for example; furthermore with increasing fineness of subdivision the Tyndall effect decreases, disappearing as molecular dimensions are approached.

Just as in the cosmic field our most powerful telescopes fail to resolve the fixed stars, which are nevertheless *visible* as points of light of varying brilliancy, so, too, in the ultramicroscopic field, we can *see* particles much smaller than the resolving power of the microscope (that is, smaller than a wave length of light) provided only that they diffract sufficient light

\* Also known as the Faraday-Tyndall effect.

to affect the retina. Based upon the experience of astronomers we may be able greatly to increase the sensitiveness of the ultramicroscope by fortifying the eye, so to speak, with the photographic plate, using at the same time tropical sunlight or ultraviolet \* light for illumination.

In the original form of the ultramicroscope, as perfected by Siedentopf and Zsigmondy, which is the one best adapted for the examination of transparent solids, a side illumination is effected by a microscope objective with micrometer movements, which throws an intense but minute conical beam of light into the fluid contained in a little cell having quartz windows at the side and top. Above this cell a compound microscope is adjusted vertically, so that the narrowest part of the light cone occupies the center of the focal plane. If the fluid under examination is optically clear or if it contains particles so small that they cannot diffract sufficient light to create a visual impression, the light cone cannot be seen. If enough light is diffracted, the light cone becomes visible, being homogeneous if the particles are too small or too close together to be individually seen, and heterogeneous if the particles can be individually distinguished. Particles or dimensions beyond the resolving power of the microscope (about  $\frac{1}{4} \mu$ ) are for brevity termed *ultramicros*. Ultramicros that can individually be made visible are called *submicrons* (or hypomicrons) while those so small that they produce an unresolvable light cone are termed *amicros*.

Knowing the percentage of gold present in a colloidal gold solution and assuming a certain specific

\* This has recently been done by T. Svedberg.

gravity and uniform shape for the gold particles, the average size and mass of a single particle of colloidal gold can be calculated, if the number present in a given volume be first counted. In this manner Zsigmondy has shown that the smallest particles of colloidal gold which can be individually distinguished with bright sunlight are approximately  $5\ \mu\mu$  in diameter, that is, five millionths of a millimeter; still smaller particles exist but they produce only an unresolvable light cone. Magnified 1,000,000 times such a tiny gold particle would be about  $\frac{1}{4}$  inch in diameter, while a human red blood corpuscle would be about 25 feet across, and a hydrogen molecule a speck barely visible. The gold particles in the unresolvable light cone must therefore closely approach molecular dimensions. In fact, by allowing amicros to grow into visibility in a suitable solution and then counting them, Zsigmondy has recently shown that some of the particles of colloidal gold have a mass of  $1-5.10^{-16}$  mg., indicating a size of 1.7 to  $3\ \mu\mu$ .

Various other types of ultramicroscopes, mainly modifications of dark field illumination, have been developed by Cotton and Mouton, Ignatowski (made by Leitz), Siedentopf (cardioid condenser, made by Zeiss) and others, and besides being useful in examining colloidal solutions, they have enabled pathologists to see and discover ultramicroscopic bacteria (spirochetes, infantile paralysis).

Bausch & Lomb Optical Co. of Rochester, N. Y., are now producing a useful ultramicroscope.

## CHAPTER 6

### GENERAL PROPERTIES OF COLLOIDS

The optical properties of colloids and their simulation of chemical compounds have been already referred to. The other general properties of colloids may be considered under the following headings:

1. Colloidal Protection.
2. Dialysis, Ultrafiltration and Diffusion.
3. Electric Charge and Migration.
4. Pectization (Coagulation) and Peptization.
5. Viscosity.

#### Colloidal Protection

Without an understanding of the underlying principles, isolated facts have long lain like individual gems scattered or even lost in the wide fields of human experience. A theory is necessary to string them together, each in its proper place, to form a beautiful necklace; or rather, a theory to serve as a matrix that forms of them a cutting drill, with which we may bore into the hard rocks of the still unknown.

Continually, throughout chemical literature, the use of protective substances crops up, only to be buried again or to be hidden in the *oubliette* of some rule-of-thumb formula. The *aurum potabile* of the alchemist was made by reducing gold chloride in the presence of ethereal oils. Then followed the use of solutions of tin which stabilized the gold sol by the stannic oxide simultaneously produced, giving the rich purplish red solution known as the *purple of Cassius*. In 1794

colloidal gold produced *in situ* was known as a dye for silk; in 1821 egg-white, isinglass, and starch were used as protectors for gold sols; and the *Lehrbuch* of Berzelius (1844) contains several recipes for producing gold sols of various shades. In 1856 Faraday \* reports the discovery of jelly (evidently isinglass or gelatin) as a protector to colloidal gold; and, finally, Zsigmondy (1898), then unaware of the preceding work, rediscovered gold sols.†

A most important contribution of Zsigmondy, however, was his demonstration that stable though highly sensitive gold sols could be made without the use of protectors provided the presence of coagulators was avoided, and also the proof that these sensitive sols could be stabilized by the addition of gelatin, gum, and the like. Then only did the full import of colloidal protection begin to dawn and the use of the principle, as such, begin to be understood and developed. Zsigmondy also synthesized the purple of Cassius by simply mixing the pure colloids of gold and stannic acid, thus proving that here the stannic acid takes the part of a protector.

Von Meyer and Lottermoser‡ had just previously recognized protective action as such, calling attention to the fact, long utilized by practical photographers, that albumin stabilized silver sols. Lottermoser§ later said that “on the addition of very stable colloids, as albumin, gelatin, agar, or gum arabic, to a silver sol, no precipitation is caused by electrolytes until the stable colloid is coagulated. The less stable silver sol

\* *Phil. Trans.*, 1857, p. 145.

† “Colloids and the Ultramicroscope,” 1909.

‡ *J. prakt. Chem.*, 56 (1897), 241.

§ “Anorganische Kolloide,” 1901, p. 50.



is thus protected against the electrolyte by the more stable colloid; it becomes more like the latter in its behavior."

### Gold Number

With his pure but sensitive ruby-red gold sols (gold content about 0.005 to 0.006 per cent), Zsigmondy then established the relative protective value of a number of protective substances. The "gold figure," compiled from the results of Zsigmondy and Schryver (see below), indicates the number of milligrams of protector which just fail to prevent the coagulative color change from red to violet of 10 cc. of the colloidal gold solution upon the addition of 1 cc. of 10 per cent sodium chloride solution. It must be remembered that the relative protective values were determined with gold, and while they are generally maintained, they may be different with other substances, especially those that coagulate the protector or adsorb it poorly. A substance fixed by adsorption often does not behave as it does when free, so that stability and protective power are not necessarily parallel functions.

SUBSTANCE	GOLD NUMBER
Gelatin	0.005 to 0.01
Russian glue	0.005 to 0.01
Isinglass	0.01 to 0.02
Casein (in ammonia)	0.01
Egg-globulin	0.02 to 0.05
Ovomucoid	0.04 to 0.08
Glycoprotein	0.05 to 0.1
Amorphous egg-albumin	0.03 to 0.06
Crystallized egg-albumin	2.0 to 8.0
Fresh egg-white	0.08 to 0.15
Gum arabic	0.5 to 4.0
Gum tragacanth	2.0 $\pm$
Dextrin	6.0 to 20.0
Wheat starch	5.0 $\pm$
Potato starch	25.0 $\pm$

Sodium oleate	0.4 to 1.0
Sodium stearate at 100 degrees	0.01
Sodium stearate at 60 degrees	10.0
Deutero-albumose	$\infty$
Cane sugar	$\infty$
Urea	$\infty$
Stannic acid sol (old)	$\infty$

Zsigmondy, following W. B. Hardy, classified colloid sols into two broad classes, based on their behavior on desiccation—the reversible or resolvable, and the irreversible or irresolvable sols. These correspond roughly with the groups hydrophile-hydrophobe (Freundlich), lyophile-lyophobic (Perrin), and suspensoid-emulsoid (Wo. Ostwald). Although some salts (citrates, sulfocyanates) may act as protectors, protection is generally accomplished by adding a reversible or emulsoid colloid to an irreversible one, which thereupon acquires reversible properties—that is, it becomes insensitive to electrolytes, redissolves after desiccation (at any temperature that does not render the protector insoluble), and passes through ultrafilters that would otherwise hold it back.

The generally accepted explanation of this phenomenon is that advanced by Bechhold,\* that the protector is adsorbed at the free surfaces of the protected particle. Zsigmondy supports this view, although he was unable to detect ultramicroscopically any sign of the adsorbed layer or any diminution in the Brownian motion. This is not surprising, as the protecting layer is probably only one or two molecules thick. Another possibility is that the protector, following its adsorption, may change the net charge of the particles.

\* *Z. phys. Chem.*, 48 (1904), 385.

Experimentally, it is a most surprising fact that certain minimal quantities of protectors actually sensitize instead of protect, and may themselves even produce flocculation. Thus, according to Bechhold,\* 0.0003 to 0.0001 parts of gelatin per million will flocculate gold sols or oil emulsions. The work of J. Billiter † indicates that this is due to the fact that in such cases the minute amount of added protector brings the other colloid to or near the isoelectric point, where, as Hardy has shown, all colloids are especially susceptible to coagulation.

From what has been said it is evident that although, in general, oppositely charged colloids precipitate each other, if an excess of a positive protective reversible (emulsoid) sol is quickly added to a negative irreversible (suspensoid) sol, the protector is adsorbed and protects before precipitation can occur. If, however, only a very small quantity of the protector is used, or, what amounts practically to the same thing, if the protector be added very slowly, precipitation may occur before protection can be established—that is, precipitation may depend upon the speed of mixing as well as on the relative proportions mixed. This gives us also an explanation of the curious “zones of precipitation” investigated by Neisser and Friedmann, H. Bechhold, Teague and Buxton, A. Lottermoser, and J. Biltz.

It is not at all strange that the behavior of a sol should be in large measure controlled by the nature of the outer layer or skin of its particles. Adhesion, as is well known, depends upon the nature of the outside layers, and so in fact does chemical action; for,

\* “Colloids in Biology and Medicine,” translated by J. G. M. Bullowa.

† *Z. phys. Chem.*, 51 (1905), 142.

while the nucleus of an elemental atom is mainly responsible for its atomic weight, its chemical behavior is governed by its outer ring or layer of electrons.

It would be a long task to discuss the numerous cases where colloids are used, wittingly or unwittingly, in scientific, medical, or technical practice, as protectors, deflocculators, and emulsifiers; or where they must be removed because their presence is detrimental. Problems of this kind abound in such widely diverse fields as photography, metallurgy, brewing, rubber, paper, glass, filtration, cooking, cement, agriculture, tanning, paints, pharmacy, biology, etc. Colloidal sols exist everywhere in the organism, and no reaction takes place there without being influenced by their presence.

To illustrate the working of protection, compare precipitates of silver chloride and tin or lead "trees" made in the presence and in the absence of gelatin, or divide a lead acetate solution into three parts, adding a little hot gelatin solution to the last. The first will give with hydrochloric acid a curdy precipitate of lead chloride; the second will give with sodium chloride (which is less highly ionized than HCl) a turbid lead chloride sol; while the gelatin-containing solution will, preliminarily at least, show no visible turbidity with sodium chloride.

Simple colloidal protection has long been known. Let us now consider some newer aspects of this remarkable phenomenon—namely, double or plural protection, autoprotection, and cumulative protection.

### Double or Plural Protection

In 1908, while experimenting with milk, it seemed that casein might be an adsorption product containing protein and calcium salts. Accordingly, an attempt was made to produce a colloidal precipitate of calcium phosphate in the presence of such protectors as gelatin and gum arabic. The protector was added first to the sodium phosphate alone and then to the calcium chloride alone; but in neither case could a precipitate be obtained which approached casein in fineness or stability.

Upon following mentally the course of the formation of colloidal calcium phosphate in the body, the idea was conceived that, since in the organism all reacting fluids hold protectors, perhaps the result could be obtained by adding some protector to *both* of the reacting solutions. The experiment was at once tried, and yielded, with gelatin as protector, a colloidal calcium phosphate which could be precipitated by both acid and rennin. Upon emulsifying some olive oil in the mixture, a stable artificial milk was obtained. Thus was developed the principle of double or plural protection, for which a U. S. patent was secured.

The literature contains several instances where this principle has been used in a more or less empirical manner. Thus, Carey Lea produced some of his colloidal silver by the following formula:

SOLUTION 1		SOLUTION 2	
Water	800 cc.	Water	800 cc.
20 per cent Rochelle salt solution	200 cc.	20 per cent Rochelle salt solution	200 cc.
40 per cent silver nitrate solution	50 cc.	30 per cent crystalline ferrous sulfate solution	107 cc.



Solution 2 was then added to Solution 1. The Rochelle salt here acts as a protector.

In the photographic field the so-called Lippmann "grainless" emulsion is made by the following formula:

SOLUTION 1		SOLUTION 2	
Gelatin	75 grains	Gelatin	75 grains
Potassium bromide	3 grains	Silver nitrate	45 grains
Water	8 oz.	Water	8 oz.

The ingredients are mixed in the order given; and after allowing the gelatin to swell, the solutions are heated to 95° F. Then Solution 2 is added to Solution 1.

Lobry de Bruyn \* found that, upon adding gelatin to both reacting solutions, precipitation may in many cases be inhibited, a colloidal dispersion resulting. Thus, under these conditions potassium bichromate and silver nitrate give a brick-red coloration but no precipitate. In general, Lobry de Bruyn used 0.1 to 0.05 *N* solutions, protecting them with 5 to 10 per cent of gelatin.

The value of this principle in producing colloidal precipitates is obvious, especially for colors, insecticides, pharmaceutical preparations, etc. It is also of the highest importance in biology and medicine, and may serve to explain many anomalies in physiology, pathology, and related branches, where things happen *in vivo* that are not duplicated *in vitro*. Almost no reactions occur in the organism which are not controlled by the protective colloids everywhere present.

\* *Rec. trav. chim.*, 19 (1900), 236; *Ber.*, 35 (1902), 3079.

### Autoprotection

Many substances are naturally prone to assume the colloidal state, and in a large number of these it appears that the molecular aggregates first reaching the colloidal degree of dispersion where surface forces predominate adsorb the less aggregated groups or isolated molecules, and thus the advance toward visible crystallization is delayed, or, for all practical purposes, entirely inhibited. Such a condition occurs in sulfur and also in pure iron, where one allotrope,  $\gamma$ -iron, seems to be adsorbed by  $\alpha$ -iron (ferrite). Ammonium salts, in particular, and some oleates exhibit the phenomenon. The globulitic stage is often a precursor to crystallization, but conditions may prevent emergence from this stage. Lactose acts this way. Several remarkable cases of autoprotection have been reported and these will be briefly considered.

W. B. Hardy \* found that 5-dimethylaminoanilino-3, 4-diphenylcyclo-1, 2-dione, upon cooling from its solutions in organic solvents, gives gels that gradually become crystalline. Gortner and Hoffmann † report that dibenzoyl-1-cystine forms even in 0.2 per cent solution a rigid gel, which in the course of several weeks crystallizes almost completely. So powerful is its gelatinization that this dilute solution makes as strong a jelly as a 5 per cent solution of gelatin. Camphorylphenylthiosemicarbazide acts similarly, its solutions in organic solvents forming, on quick cooling, gels that gradually become crystalline.‡

\* *Proc. Roy. Soc. (London)*, **87A** (1913), 29.

† *J. Am. Chem. Soc.*, **43** (1921), 2199.

‡ Forster and Jackson, *J. Chem. Soc.*, **91** (1907), 188; E. Hatschek, *Kolloid Z.*, **11** (1912), 158.

### Cumulative Protection

The general rule in colloidal protection is that anything which removes, coagulates, or destroys the protector, or disperses it crystalloidally, will cause the protected dispersion to coagulate. Thus, on adding ferric chloride to olive oil emulsified with gum arabic, the gum is coagulated and loses its emulsostatic action, so that the oil separates out—the emulsion “breaks.” On the other hand, anything that protects the protector—that is, stabilizes it against coagulation, crystalloidal dispersion, or destruction—will tend to stabilize the protected sol. Thus, some ammonia in a gelatin-protected sol would tend to prevent the coagulation of the gelatin by formaldehyde, and an antiseptic would prevent its dispersion by bacteria or enzymes which, as the work of E. Zunz indicates, may convert protectors into coagulants. The rennin coagulation of milk seems to be of this nature, the enzyme converting the protective lactalbumin into a coagulant.\*

This introduces a new idea—cumulative protection. In many cases we must expect to find that the protector of the protective colloid is itself a colloid, and there is no reason to doubt that cumulative protection may extend through a series of several colloids, or colloids and crystalloids, giving a structure which, like a house of cards, may collapse if any one of its essential supports is removed.

This aspect of protection does not seem to have been recognized or investigated experimentally as such, and it offers a wide field for research. As instances of its practical operation may be mentioned glasses, alloys,

\* Alexander, *8th Intern. Cong. Appl. Chem.*, 1912.

and the gluten of wheat and rye flours. Many protein and similar complexes may be built up in this fashion.

### Dialysis

Colloid solutions possess a small but definite diffusibility through colloidal septa (parchment paper, bladder) as was recognized by Graham, who found that "tannic acid passes through parchment paper about 200 times slower than sodium chlorid; gum arabic 400 times slower." \* Graham's original form of dialyzer may be made from a wide-mouthed bottle whose bottom has been removed.† The mouth is closed by a piece of bladder or parchment paper tightly bound on, the solution to be dialyzed is poured in, and the bottle immersed about halfway in water contained in a larger vessel. Most of the crystalloids diffuse through the membrane into the outer water, which should be frequently renewed, while most of the colloids remain in the original bottle, and may be thus obtained in a purified condition. Improved modern dialyzers consist of parchment or collodion sacs or thimbles, or even of whole bladders, which have the advantage of a larger dialyzing surface.

### Ultrafiltration

H. Bechhold found that he could make filtering membranes of varying degrees of permeability by forming them from jellies of varying concentration. He used principally collodion dissolved in glacial acetic acid and afterward immersed in water, and

\* It is commonly but erroneously stated, even in text books, that colloids do not diffuse or dialyze. The extent to which dialysis occurs depends mainly on the fineness of the colloidal particles, the nature of the septum, and *time*.

† A lamp chimney will answer very well.

gelatin jellies hardened in ice-cold formaldehyde. The jellies were formed and hardened on pieces of filter paper, which were supported from below by nickel wire cloth, and clamped between two flanges. The liquid to be subjected to ultrafiltration is introduced in the chamber thus formed and forced through the prepared septum by appropriate pressure, which may run up to 20 atmospheres or more and may be produced by a pump or by compressed gas (air, nitrogen or  $\text{CO}_2$ ). Table VII (below), prepared by Bechhold, shows various colloids arranged in order of the diminishing size of their particles in solution, and

TABLE VII

Suspensions.

Prussian blue.

Platinum sol (made by Bredig's method).

Ferric oxid hydrosol.

Casein (in milk).

Arsenic sulphid hydrosol.

Colloidal gold hydrosol (Zsigmondy's No. 4, particles about  $40\ \mu\mu$ ).

Colloidal bismuth oxid (Paal's "Bismon").

Colloidal silver (Paal's "Lysargin").

Colloidal silver (von Heyden's "Collargol," particles about  $20\ \mu\mu$ ).

Colloidal gold hydrosol (Zsigmondy's No. 0, particles about  $1-4\ \mu\mu$ ).

Gelatin solution, 1 per cent.

Hemoglobin solution, 1 per cent (molecular weight about 16,000).

Serum albumin (molecular weight about 5000 to 15,000).

Diphtheria toxin.

Protalbumoses.

Colloidal silicic acid.

Lysalbinic acid.

Deuteroalbumoses *A*.

Deuteroalbumoses *B* (molecular weight about 2400).

Deuteroalbumoses *C*.

Litmus.

Dextrin (molecular weight about 965).

Crystalloids.



was obtained by using ultrafilters of varying degrees of porosity or permeability.

By means of ultrafiltration through ultrafilters of appropriate permeability, not only may colloids be separated from crystalloids, but colloids having particles of different sizes may be separated from each other.

### Diffusion

Diffusion through a septum is, of course, involved in dialysis. If, however, diffusion occurs *into a jelly*, many interesting phenomena may develop, especially if the jelly adsorbs any of the diffusing substances or contains substances which can react with them.

Owing to the enormous surface they present, colloidal gels exhibit a powerful adsorptive action. In fact, even when percolated through such a relatively coarse-grained septum as sand, most solutions issue with a materially reduced content of solute, and benzopurpurin solutions may be thus decolorized. Further, if a solute hydrolyzes into ions having different degrees of adsorbability or different rates of diffusibility, they may be actually separated by diffusion through a colloidal gel.

This phenomenon is nicely exhibited by what may be termed a "patriotic test tube," prepared by filling a tube about two-thirds full with a slightly alkaline solution of agar containing a little potassium ferrocyanid and enough phenolphthalein to turn it pink. After the agar has set to a firm gel, a solution of ferric chlorid is carefully poured on top, and almost instantly the separation becomes evident. The iron forms with the ferrocyanid a slowly advancing band of blue, before which the more rapidly diffusing hydrochloric

acid spreads a white band as it discharges the pink of the indicator. After the lapse of a few days the tube is about equally banded in red, white, and blue.

Even then the tubes do not cease to be of interest, for if they are allowed to stand several weeks the pink color is all discharged and there develop peculiar bands or striations of blue, apparently due to the fact that the iron ferrocyanid temporarily blocks the diffusion passages, which are gradually opened again after a layer of the blue salt has diffused on from the lower surface. (*Liesegang's rings*.\*)

Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel or septum. (*Differential Diffusion*.)

### Electric Charge and Migration

The particles of practically all colloidal solutions possess an electric charge, and under the influence of an electric current (difference of potential) move toward the electrode having the opposite charge. (*Electrophoresis*.) In general, when two substances are brought into contact, the one having the *higher* dielectric constant becomes *positively* charged, whereas the one with the *lower* dielectric constant becomes *negatively* charged (Cohen's Law). Since water has a high dielectric constant (80), most substances suspended in pure water become negatively charged and wander to the anode. On the other hand, if suspended in oil of turpentine, which has a low dielectric constant

\* Liesegang's rings, named after Raphael Ed. Liesegang, are of importance in mineralogy (agates), geology (ore deposits), and biology (rhythmic banded structures).

(2.23), they become positively charged and wander to the cathode.

If, however, electrolytes are present, Cohen's law is superseded by other controlling factors, such as the adsorption of ions, which may give their charge to the suspended particles. In fact Hardy found that in pure water albumin was amphoteric; in the presence of a trace of alkali it acquired a negative charge and migrated to the anode; but a trace of acid gave it a positive charge and it then migrated to the cathode. The following table shows the usual charge and migration tendency of a number of *aqueous* colloidal solutions.

Charged + Migrate to Cathode (− Pole)	Charged − Migrate to Anode (+ Pole)
1. Hydrates of Fe, Cu, Cd, Al, Zr, Ce, Th.	1. Sulphids of As, Sb, Cu, Pb, Cd. Halides of Ag.
2. Titanic acid.	2. Stannic acid, silicic acid.
3. Colloidal Bi, Pb, Fe and Cu (Bredig's method).	3. Colloidal Pt, Au, Ag, and Hg, I, S, Se.
4. Albumen, hemoglobin, agar.	4. Gum arabic, soluble starch, gamboge, mastic, oil emul- sion.
5. <i>Basic Dyes</i> : Methyl violet, Bismarck brown, methylene blue, Hofmann violet.	5. <i>Acid Dyes</i> : Eosin, fuchsin, anilin blue, indigo, soluble Prussian blue.

The electrically charged particles tend to, and usually do, surround themselves with ions of the opposite charge, forming thus an *electric double layer*, as it is called. Or polar molecules may be oriented at the interface between the particle and the dispersion medium.

### Pectization and Peptization

Briefly stated, pectization means the coagulation of a colloidal sol, and peptization its redispersion. If a small quantity of an electrolyte is added to a pure ruby red colloidal gold solution, the latter changes to a blue or violet color, and deposits its gold as a fine blackish coagulum or precipitate. By watching in the ultramicroscope the coagulation of very dilute milk by dilute acid, the individual particles of the colloidal casein may be seen to gather gradually together into groups, whose motion becomes progressively less as their size increases, until they are no longer able to stay afloat, and finally coagulate in large grape-like clusters. Hardy believes that the particles of colloids adsorb the oppositely charged ions of electrolytes present; at the *isoelectric point* (that is, when there is no excess either of positive or negative charges on the particles) coagulation occurs. If, however, an *excess* of electrolyte be added *all at once*, the isoelectric point may be passed before coagulation occurs, and the particles acquire a charge opposite to the one they had originally. Under such conditions, no coagulation may result.

Burton epitomizes the difference in action of various electrolytes as follows: "Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle; and, second, with solutions of salts, trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalis in particular cases act more strongly than the corresponding salts."



High-tension electric discharges may also effect the coagulation or precipitation of a finely subdivided or dispersed phase; which fact was utilized by Sir Oliver Lodge in dispelling fogs, and by Cottrell in coagulating smelter and similar fumes.

*Peptization.*—So strong is the analogy between digestion and colloidal disintegration that Thomas Graham, the father of colloid chemistry, coined the word *peptization* to express the liquefaction of a gel. He first speaks of the coagulation or peptization of colloids. "The peptization of liquid silicic acid," he states, "and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may be again liquefied, and have its energy restored by contact with very moderate amounts of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100 degrees. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids in such circumstances may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron and titanin acid,



prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

Peptization is in reality deflocculation, a dispersion of groups into separate particles which once more acquire active motion and remain afloat or in solution. The detergent action of soap and dilute alkalis is due to the fact that they deflocculate adhering particles of "dirt."

### Viscosity

Viscosity depends largely on the relation between kinetic motion and free or specific surface. It may be measured by time of flow from an orifice under a fixed head or pressure (Ostwald or Engler types), or by measuring the force needed to shear layers of liquid past each other (Couette or MacMichael types). Crystalloid solutions exhibit low viscosity; the rapid motion of their particles aids flow. The relatively coarse suspensions are likewise not viscous, because of deficiency of active surface. In the colloidal zone we find maximum viscosity, which falls off on either side (zone of maximum colloidalinity, see p. 16 et seq.).

Slowly moving particles exhibit inertia to the commencement of flow, and this accounts for what is known as "plasticity" or "yield value" of viscous materials. Theoretically everything should have some yield value, though in many cases it is not measurable, especially over limited time.\*

\* See J. Alexander, "Glue and Gelatin," p. 98 et seq.

Thomas Graham said (Proc. Roy. Soc. Lond., 1864): The ultimate peptization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid transpiration-tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

## CHAPTER 7

### PRACTICAL APPLICATIONS OF COLLOID-CHEMICAL PRINCIPLES

The practical applications of colloid chemistry are so manifold and widespread that they touch every branch of science and technology. Whole books may be and have been written on many of the most restricted fields, while the scientific literature teems with monographs and articles, directly on, or applicable to, colloid-chemical subjects. In what follows, it will be possible therefore to give not an exhaustive, but only a most general survey, intended primarily to show the ubiquity of colloid phenomena; and many important topics must be dismissed with a most rudimentary discussion, altogether incommensurate with their importance.

Practically all the substances we meet with in our everyday life are colloids, and we are mainly colloids ourselves. The foods we eat, the clothes and shoes we wear, the wooden furniture we use, the houses we live in with their windows, carpets and floors, the metals and rubber of our automobiles as well as their leather or leather substitutes, the very books and newspapers we read, and the paper and twine that our purchases come wrapped in—all are largely if not entirely composed of colloids or matter in the colloidal condition. Consequently, problems in colloidal chemistry appear in every branch of science, industry and technology.

It is intended here to give in outline a sketch of a number of these applications, stressing more particu-

larly those that have biological technological bearings, but including others that show the operation of the colloid-chemical principles involved. In order to bring some coherence into this extensive survey, the topics are gathered into more or less related groups as follows:

## I

Astronomy  
Meteorology  
Smokes and Dusts  
Perfumes

Geology  
Mineralogy  
Gems

## II

Agriculture  
Clay

Ceramics and Refractories  
Flotation

## III

Dyeing  
Shower-proofing of  
Fabrics

Nitrocellulose and Its  
Products  
Paints, Pigments and Var-  
nishes  
Emulsions

## IV

Soaps  
Lubrication  
Coal  
Colloidal Fuel

Petroleum  
Asphalt  
Fire Foam  
Insecticides

## V

Filtration  
Sewage Disposal  
Photography

Brewing  
Tanning  
Paper  
Rubber

## VI

Foods	Ice Cream
Baking	Confectionery
Milk	Gelatin and Glue

## VII

Glasses	Boiler Scale
Metals and Alloys	Cement, Mortar and Plaster
Electro-deposition of Metals	

## VIII

Chemical Analysis	Antiseptics and Bacteriology
Pharmacy and Therapeutics	Biology and Medicine

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**Astronomy**

As matter in colloidal state is so common on our relatively minute earth, it is but natural to expect to find many instances of colloidal dispersion in the immensity of the Universe.

Cosmic dust is widely distributed throughout space, and as it is gathered up by the superior attraction of the larger heavenly masses (suns, planets, etc.), which in any system grow at the expense of the smaller masses, fresh quantities are continually produced by the collisions of bodies in space, as well as the disintegration of meteorites, comets, asteroids, etc.

According to Isabel M. Lewis of the U. S. Naval Observatory, a swarm of meteors or "shooting stars" (which are quite different from the large meteorites or fire balls) consists of minute dust-like particles which for the most part do not weigh as much as a

single grain. If we could view them outside our atmosphere, they would appear as a cloud of dust reflecting the sunlight, their luminescence being caused by the friction of their rapid passage through our atmosphere. Particles of colloidal size, which probably accompany them through space, tend to be retarded by the viscosity of our atmosphere.

The zodiacal light also seems to be consequent on a cloud of colloidal matter generally believed to surround the sun. Lars Vegard recently advanced the view that the upper atmosphere contains minute crystals of frozen nitrogen, to which he attributes the blue color of the sky, as well as the aurora borealis and the zodiacal light (see *Philosophical Transactions*, Oct. 1923).

When enormous nebulous or fluid masses moving through space approach each other, they cause huge "tides" in each other, and as the bodies pass, these tides are converted into swirls (spiral nebulae) which may later condense into planetary units about the residual central sun (solar system). This view accounts for the fact that our planets all revolve in one direction, and it furthermore allows for the persistence of colloiddally dispersed residues, as well as "captured" matter. The retrograde moon of Jupiter is probably a "captured" satellite.

Heavenly bodies must occasionally meet in collision, and the terrific impact must add to the nebulous or cometary masses of colloidal matter which are distributed throughout space.\* While most of these bodies

\* In contradistinction to phenomena of such magnitude Prof. R. A. Millikan (Nobel prize winner) weighed the electron by catching these minute individual particles of negative electricity on colloidal oil droplets which he viewed in an ultramicroscope.



are self-luminous, others are lighted up by neighboring suns. Light itself is invisible, but a beam of sunlight shot into a darkened room becomes evident by illuminating the innumerable motes in our atmosphere, most of which are colloidal. Some of these atmospheric nuclei, as C. T. R. Wilson has shown, are due to the deposit of moisture, etc., on ions or ionized particles, but others are without charge.

A few years ago when, as astronomers had foretold, the earth was about to pass through the tail of a comet, our yellow journals warned us to prepare for the end—but no one, not even the astronomers, noticed the slightest effect. The tail, whose length ran into millions of miles, was only a vast cloud of colloiddally dispersed extremely tenuous matter, and its luminosity was simply a Faraday-Tyndall effect on a gigantic scale, but analogous to the beam which a searchlight or automobile headlight shoots through the atmosphere, especially if it is slightly hazy. The spectroscope indicates that the luminosity of the tail is due to reflected sunlight.

The tails of comets seem to consist almost entirely, and the nuclei and coma largely, of colloiddally dispersed matter. The great comet of 1882 which made a transit of the sun was invisible against the solar disc (a position corresponding to attempted observation of colloidal particles in the ordinary microscope against a luminous background), but became visible again after passing beyond the sun's disc (a position corresponding to successful observation of the same colloidal particles in the ultramicroscope against a dark background, the eye of the observer being protected from the source of illumination).

The streaming of the cometary tails away from the sun may be due to the ionization of the constituent colloidal particles, and their consequent electrical repulsion. With colloidal particles the Brownian or kinetic motion is a factor to be reckoned with. J. Clerk Maxwell pointed out (1870) that the intensity of the action of the sun's rays on a particle depends upon its *surface*, which varies as the *square* of its diameter, whereas the gravitation of the same particle to the sun depends upon its *mass*, which varies as the *cube* of its diameter. Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm. ( $= 1.5 \mu$ ). As the diameter diminishes, the repulsive force gains the ascendancy, soon reaching a maximum and again diminishing, until when the particle has a diameter of only 0.00007 mm. ( $= 70 \mu\mu$ ) the two forces again balance each other.\*

These figures, which refer to a substance having the density of water, are approximately of colloidal dimensions; but in the case of denser bodies the subdivision would be even more profound. It is therefore not surprising that, when the earth recently passed through the tail of a comet, no disturbance of any kind was noticed. The comet's tail is a vast celestial camouflage—its luminosity a macroscopic Faraday-Tyndall effect. From what is stated above we should imagine that in some cases the tail of a comet may point *away* from the sun, providing that its particles are of the proper size, and in fact Baade's comet, recently visible, showed this phenomenon. Comets have been seen

\* See Simon Newcomb's article on "Comet," *Encyclopedia Britannica*, 11th edition. Also Svante Arrhenius, "Worlds in the Making," Harper & Bros.

with tails pointing both towards the sun and away from it.

The nebulae, too, apparently consist of finely dispersed matter, rendered luminous by neighboring suns; although with them, as with the comets, part of the light may result from self-luminescence (incandescent gas, etc.).

### Meteorology

What we commonly call "weather conditions" are largely dependent upon the degree of dispersion of water in the atmosphere, and this dispersion is mainly effected and maintained by solar heat and electrical energy. When air carrying water vapor is chilled by rising to a higher level (which means reduced pressure and expansion), meeting a colder mass of air, or even by the alternation of night and day, the moisture it contains assumes the colloidal state as cloud, fog or mist; and as the coagulation of the dispersed water proceeds, these in turn may condense still further into dew, rain, snow or hail, depending upon conditions.

When steam under pressure blows off into the atmosphere, it appears clear some distance from the point of issue and does not become visible until it has condensed into colloidal dimensions. Then as its particles condense still further to drops (or else evaporate or are dispersed), it becomes invisible once more. White cloud particles are already larger than strictly colloidal size.

As the water particles in a cloud aggregate, the total specific or "free" surface diminishes, but must continue to hold the total electric charge because the charge distributes itself superficially. This means

that the charges on the outside of the individual droplets increase enormously until the lightning discharge occurs.\* We have all noticed how a nearby lightning flash is promptly followed by an increased fall of raindrops whose condensation gave it birth. The condensation of the moisture particles usually shows itself by the cloud assuming a dark gray or bluish-black shade.

Many water droplets are formed about ions or electrons and carry an electric charge. As the droplets aggregate the charge accumulates on the outer surface, so that in a large cloud, with an enormous number of droplets, very high potentials may result. Indeed if the aggregation of the water droplets is not sufficient to obscure the sky, and the charges are very numerous, we may have a "bolt out of the blue"—not an uncommon phenomenon.

We do not know to what extent electrical conditions on the earth affect the dispersion of substances in its atmosphere; but since half of the earth is always heated by the sun while the other half is cooler, thermoelectric currents are continually circulating about the earth. Variations in solar radiation, due to sun-spots and the like, cause violent electric and magnetic storms which are intimately connected with the aurora, and other atmospheric phenomena (ionization, electrical charge of dispersed particles).

Colloidal ice often occurs at high levels and may be the cause of halos, perihelions and periselenes ("sun-dogs" and "moon-dogs"), etc. In many elevated regions (Idaho) there occur frost fogs called by the

\* It is possible that in the gymnotus and other "electric fish," an aggregation of colloids in their special glands, due to nervous influences, may underlie the high potential and shock.



Blackfoot Indians "pogonip" or "white death," where finely divided ice, like hoar-frost on a gigantic scale, deposits on trees in huge masses, and is a contributing cause of pneumonia.

Since changes in barometric pressure must affect the  $\text{CO}_2$  tension of the blood and tissues, and since this means a variation in the turgidity of the body colloids which incidently affects the circulation (see p. 184), we have here one basis for the popular impression that the "weather" influences our feelings. Other factors are of course at work (e.g., evaporation of water from the skin, etc.), but physicians know that with persons suffering from neurotic and rheumatic affections, the effects of weather conditions are noticeable. Change of altitude may have a similar effect.

The blue color of the sky is caused by diffraction of the sunlight by the earth's atmosphere. Were it not for this gigantic Faraday-Tyndall effect the sun would appear to us as a fiery ball set in a black star-sprinkled sky. The varying shades of bodies of water ("blue Mediterranean," "green" ocean, black, yellow, white, red rivers, etc.) are largely due to the diffraction caused by finely dispersed substances. When we look through a great length of the atmosphere, distant objects such as mountains seem to have a blue tone.

'Tis distance lends enchantment to the view,  
And robes the mountain in its azure hue.

So the poet Thomas Campbell beautifully puts it in his "Pleasures of Hope." Though atmospheric gases exercise some effect, without colloidal dust we would have less romantic twilight, and darkness would fall rather sharply as the sun sank below the horizon.



The blue-whiteness of snow, which sometimes even assumes a positive blue tint, is due to the reflection of light from its interior surfaces, the color being a structural one. [See J. Alexander, *Science*, 41, 465 (1920).] As Bancroft has pointed out, the blue color of many birds' feathers is due to their colloiddally fine structure. A certain green tree toad owes its color to a structural blue, which on passing through a layer of yellow oil droplets in the skin appears green. If preserved in alcohol, which dissolves out the oil, the toad turns blue.

The tremendous explosive eruption of the volcano Krakatoa in 1883 projected colloidal dust and ashes so high that they gradually spread entirely around the earth. Besides causing glorious "golden sunsets," such fine dust is by many believed to exert a noticeable influence upon weather conditions. While many particles in such dust greatly exceed colloidal dimensions, it must be remembered that the effects of fine subdivision do not end abruptly with the usual colloidal limits of 5 to 100 millimicrons. Test plates taken in an airplane, show that pollen grains are numerous at an altitude of 15,000 feet (Hay fever).

One more curious function of colloidal atmospheric dust must be mentioned. As Kendall has shown, the proper functioning of the thyroid gland depends upon the presence of a small quantity of thyroxin, an iodine-containing organic compound. This means that iodine must be found in traces in the soil, from which all food directly or indirectly comes. The original source of iodine is the sea, and although some of it exists in geological deposits of sea salt, a continual source of supply to the soil is to be found in the col-

loidal sea-salt dust, which forms from the ocean's spray and is carried thousands of miles inland before being washed down by the rain. The incidence of goiter and cretinism (largely due to iodine insufficiency) is most marked in interior mountainous (Switzerland, Idaho, Wyoming) regions where the least amount of sea-salt dust is apt to be carried. Thus it would take a person 1,000 years to drink enough of the water of Lake Superior to give the iodine needed for his thyroid gland.

### **Smokes, Fogs and Dusts** (Aerosols)

Fogs, mists, and clouds, whether of water or dust, exercise a potent influence on terrestrial climate, flora and fauna, for they govern to a considerable degree the amount of solar radiation reaching the earth's surface. According to one theory, glacial periods were, in part at least, due to such influences.

By interfering with the normal passage of solar radiations, as well as by furnishing nuclei for the deposit of moisture to form fog, coal smoke, if present on a large enough scale (as in some parts of England), may exert an effect upon weather conditions. Carl Barus [Smithsonian Contribution 1309 on "Atmospheric Nucleation," Washington, 1905] kept a continuous record of atmospheric nucleation for several years and found that the number of nuclei varied from about 2,000 to 100,000 per cubic centimeter. Such nuclei may be produced by violently agitating liquids, by heated bodies (red-hot metal or glass, a clear non-luminous bunsen flame), by chemical activity (smokeless oxidation of phosphorus at about 13 deg.), by evaporation (e.g., of sulphuric acid or naphthalene), by

high potential (charged metal), and by certain kinds of radiation (ultra-violet light, X-rays, radioactivity). Barus says that the nuclei are at the outset simply dust particles small enough to float in the air, but larger than the order of molecular size, upon which water condenses. Most of them carry an electric charge. Atmospheric nucleation varied greatly from day to day and during the day, but was on the average greatest at the winter solstice (December 21) and least at the summer solstice (June 21).

In flames, the burning matter is largely in colloidal state, and when a combustible dust suspended in air approaches colloidal dimensions, its free surface becomes so great that it may burn with extreme rapidity if started by a static or frictional spark or the like (*explosive aerosols or dusts*).

Sodom and Gomorrah were probably destroyed by a colloidal cloud of petroleum ignited by local fires or lightning. Analogous phenomena are known in the Caucasus Mountains to-day.

The electrical precipitation of colloidal and finely dispersed substances from air, smoke, furnace gases, etc., by the Cottrell process is too well known to be described in detail here. Unexpected sources of profit are being found in the fumes compulsorily collected from cement kilns (potash) and from smelters (arsenic, selenium, etc.). Many dusts and mists (including sulphuric acid, which is a very good nucleator) that had defied ordinary bag-house methods are readily separated out by the high tension current. Sir Oliver Lodge even suggested that ships might thus clear their path of fog for some distance ahead.

Recently W. D. Bancroft and L. F. Warren demon-

strated that electrified sand, scattered by an airplane, could cause the coagulation of fog and clouds, thus producing even a slight localized "rain."

One case where smoke is intentionally produced is in the use of "smudge pots," which are burned in orchards in the spring or early summer when indications are that the tender blossoms or fruit are about to be injured by frost. This remedy is, of course, ineffective in very cold weather, but often serves to prevent what agriculturists term a light frost, which has for its precursors a still, clear atmosphere and a temperature approximating the freezing point. Frosts of this kind do not occur on cloudy or windy nights.

In the absence of smoke, the freezing process seems to proceed as follows: With falling temperature frost may deposit directly, or a dew-like deposit of water forms on leaves, buds, fruit and similar surfaces, and is congealed into ice crystals or "frost" when the slight heat liberated by the condensation radiates into the surrounding cold atmosphere; the freezing is facilitated by the evaporation of part of the deposited water. While the heat generated by the burning smudge oil is a large factor, the smoke liberated furnishes throughout the entire lower atmosphere innumerable nuclei upon which moisture deposits, with the liberation of some heat and the formation of a protective fog blanket that tends to check terrestrial radiation. The combination of all these factors is usually sufficient to ward off the threatened calamity.

These views are strengthened by the observations of Lieutenant B. H. Wyatt (Science, Sept. 21, 1923, p. 223) who, during the recent total eclipse of the sun, took observations while flying in an airplane in a



comparatively clear layer at an altitude of 13,000 ft. "During totality the recording thermometer at this altitude showed a rise of three and one half degrees Fahrenheit instead of the anticipated drop period. The humidity fell from sixty-three to fifty-two per cent." This seems to indicate a liberation of heat upon the condensation of moisture, providing he did not enter a different stratum of air.

The recent war resulted in an enormous development of the use of artificial smokes and fogs in military and naval offensive and defensive operations. While in the old days attacks or retreats had often been made under cover of natural fog or mist, now soldiers crept to the attack under the protection of a smoke barrage, and on sea destroyers laid down a smoke screen, or steamers sought, like the cuttlefish, to escape submarines in colloidal clouds of their own making. In the air natural clouds were lurking places for airplanes and dirigibles, and many air craft, especially Zeppelins, produced colloidal clouds in which they were lost to view.

### Perfumes

Without attempting to go into the question of what constitutes the sense of smell from a nervous or psychological standpoint, it may be said that the sensation of smell or odor is aroused only by the transmission of material particles which must be very small, since they pass readily through paper, textiles and the smallest crevices, and are held back only by airtight surfaces like glass or metal. Some gases have distinct odors, but from the fact that Barus ["The Structure of the Nucleus," Smithsonian Contribution 1373,



Washington, 1903] was able to demonstrate the presence of colloidal nuclei in gasoline, benzol and carbon disulphide vapors, it is obvious that the presence of such particles is much more common than has been believed. It is a question whether these nuclei arise from molecular association or from the condensation of vapor on smaller atmospheric nuclei. The persistency of naphthalene nuclei and their tendency to reach a fixed diameter led Barus to remark that "it is probable that the vapor pressure of naphthalene, however small, is the cause of this long maintenance of the supply of nuclei, and one may suspect that other bodies with strong odors and which show a tendency to slow sublimation will be found in like degree nuclei-producing."

Ambergris evidently owes its body-producing effect in perfumes to the formation by it of nuclei which have the power of strongly condensing the vapors of the ethereal oils, etc., which constitute the odoriferous ingredients of perfumes. Thus Barus found that paraffin nuclei, made by shaking a benzol solution of paraffin, disappeared with relative rapidity. This field offers an interesting vista of research, which may lead to a cheaper or superior substitute for ambergris, among other things.

In modern society, smell is a sense that is largely *tabu*, although throughout the whole animal kingdom it is of prime importance and utility. Wild animals are guided largely by it, and insects seem to be also. While some odors are due to molecularly dispersed particles, in many cases we have to deal with colloidal particles; and it will be of interest to investigate the permeability of septa to smells. The odors of many

substances are due to impurities. Thus absolutely pure sulfuretted hydrogen, carbon disulfide and phenol are without marked odor, as are also pure indol and skatol.

### Geology

Coming back to solid earth, let us consider the ordinary properties and behavior of the earth's solid constituents. These depend more upon their state of physical dispersion than upon their chemical constitution, as may be seen by considering Atterberg's classification of minerals according to the size of their fragments:

		Diameter		
Boulders.....	2	m.	to 20	cm.
Pebbles.....	20	cm.	to 2	cm.
Gravel.....	2	cm.	to 2	mm.
Sand.....	2	mm.	to 0.2	mm.
Earth.....	0.2	mm.	to 0.02	mm.
Loam.....	0.02	mm.	to 0.002	mm.
Clay.....		smaller than 0.002 mm.		

The finer particles are more readily blown about by the wind and carried and deposited into sedimentary beds by water; they are more soluble and are more easily leached and decomposed by "weathering." In mass the finer particles are less permeable to water, but possess a much higher capillarity and water-holding capacity, besides a powerful fixing or decomposing action on diffusing substances. Thus if dilute potassium sulphate solution is percolated through a column of fine sand, free sulphuric acid is found in the percolate.

Fine deflocculated clay is carried thousands of miles by rivers, and when finally coagulated by the salts of the ocean forms new land. Geological evidence shows

that this process has added about a thousand miles to the length of the Mississippi River, and owing to the enormous areas under cultivation (which permit more soil to be carried off) it is going on perhaps faster than ever. Its results may be seen at the mouth or delta of every large river—the Nile, Ganges, Hwang-Ho, Amazon, Euphrates. The great weight thus accumulated at certain weak places in the earth's crust may cause slip along lines of geological fault. The recent (1923) destructive earthquake in Japan is believed to have had such an origin.

Fine particles generally have been deposited in huge thick beds by glacial and other prehistoric waters, which have mostly graded them according to size. Such deposits, when cemented by pressure, dehydration or igneous or metamorphic action, became slate, shale, sandstone, etc. When they enclosed pebbles, the result was "pudding stone," and these frequently served as a matrix for fossils and as a means to preserve fossil footprints, ripple marks, and even rain splashes.

Eozoon, long thought to represent the fossilized remains of primeval plant life, is probably nothing but an instance of rhythmic precipitation (Liesegang's rings), which often occur when precipitates are formed by diffusion into colloidal gels.

### Mineralogy

Agates, onyx and dendrites are types of minerals formed by rhythmic precipitation (Liesegang's rings), and ore bodies may be deposited by similar segregating action. Some minerals are themselves colloidal gels (e.g., opal, flint, bauxite) or result from other minerals

by weathering with subsequent gel formation (e.g., kaolin from kaolinite, serpentine from diabase). Lehner has recently shown that mere trituration is sufficient to bring silica into colloidal solution, and it seems that many quartz minerals have been deposited, in part at least, from colloidal solution. The same applies to stalactites and stalagmites, for with a fluctuating carbon dioxide content, especially in the presence of protectors like humus, some colloidal calcium carbonate will be formed.

### Gems

Many gem stones owe their beautiful colors to impurities colloiddally dispersed in them—the emerald to chromium, the ruby to iron, the amethyst probably to manganese, the topaz to iron, etc. The varying shades of diamonds seem to be due to similar causes. Opals are gels with interior reflecting planes. The shade and even the color of many gems can be changed by subjecting them to the action of X-rays or radium, which apparently act by bringing the dispersed particles into a different state of aggregation, usually coarser.

Pearl scales, when examined in the dark field, show the inhibited crystallization characteristic of crystals formed in the presence of a protective colloid, which here is the slime or mucin of the mollusc. There is no reason to doubt that colloid research will lead to the synthetic production of mother-of-pearl, and perhaps even of substitutes for the real pearl itself.

Since the writing of the above there has appeared in "*Chemie et Industrie*," Vol. 8, p. 782 (1922), a paper by Clément and Rivière, describing the production of artificial mother-of-pearl.

## CHAPTER 8

### PRACTICAL APPLICATIONS (Continued)

#### AGRICULTURE

Although from time immemorial farmers have classified soils on the basis of their physical and physiological character as "light" or "heavy," "rich" or "poor," "productive" or "unproductive," etc., it is only within comparatively recent years that chemists have begun to realize the full importance of the rôle played by the colloids, especially the organic colloids of the soil.

The constituents of the soil fall into three classes:

1. Mineral fragments, consisting mainly of silica and silicates, resulting from the disintegration of rocks by weather, water, heat, freezing, etc.

2. Organic material, including bacteria, and that mixture of plant and animal debris known as humus.

3. Soil solution, which is water with its various solutes.

The fact that colloids occur in all three of these classes should serve to reconcile the older hypothesis that the colloidal behavior of clay is due to fine particles, with the more recent view that it is due to a jelly-like "ultra-clay" which surrounds the particles. Both conditions exist and exert an influence. The "ultra-clay" evidently consists largely of colloidal humus, for the smallest particles, with which it exhibits its main effects, have the largest percentage of organic matter.

Among the natural agencies tending to increase the size of the minute soil particles may be mentioned



heat with its drying or evaporative effect, freezing, and the coagulating or flocculating action of soluble inorganic salts and some organic substances present in the soil. On the other hand, included in that little known class of substances vaguely described as "humus," there are numerous organic substances derived from the bacterial, plant, or animal debris, or exuded by the roots of plants, which act as protective colloids (*Schutzkolloide*) and tend to produce and maintain the hydrosol, or deflocculated condition. (See P. Ehrenberg, "Die Kollide des Ackerbodens," *Zeits. angew. Chem.*, 1908, 41, 2122.) In an excellent paper on the mechanics of soil moisture, L. J. Briggs (U. S. Dept. of Agric., Bureau of Soils, Bull. No. 10, 1897) pointed out that very small quantities of certain organic substances, such as are continually being produced in the soil by the decay of organic matter, greatly decrease the surface tension of solutions, thus counteracting to a large extent the effects of the surface application of soluble salts which would tend to draw moisture to the surface by increasing the surface tension of the capillary water of soils. It is well known, however, that an excess of salts will ruin a soil physically, as is evident after flooding by sea water or the excessive application of chemical fertilizers. Of interest in this connection is the recent work of the Bureau of Soils, U. S. Department of Agriculture, carried out by Cameron, Schreiner, Livingston, Gile, Davis, and their co-workers. Thus plants grown in the unproductive Takoma soil were greatly benefited by green manure, oak leaves, tannin and pyrogallol. The injurious effects of quinone and some other organic substances may be due to their ability to precipitate

or flocculate the protective colloids of the soil; for as Lumière and Seyewetz have shown (Bull. Soc. Chim., 1907, 4, 428-431; J. S. C. I., 1907, 703), quinone renders gelatin insoluble.

The fact observed by Fickenday (J. Landw., 1906, 54, 343) that more alkali is required to flocculate natural clay soils than kaolin suspensions, he attributes to the protective action of the humus present (see Keppeler and Spangenberg, J. Landw., 1907, 55, 299).

Many factors oppose the agriculturally undesirable tendency of humus to deflocculate clay, which would permit the rain to wash it away: (1) In suitable concentrations humus and clay act as oppositely charged colloids, and mutually precipitate each other; (2) the lime present in most soils forms with the humus a gel of the insoluble calcium humate, which sticks the soil particles together. Generally an excess alkalinity produces humus soils and the evil effects found in the heavy, sticky alkali soils.

When all these factors are properly balanced, the soil is in good *tilth*, which Sir E. J. Russell defines as that "nice crumbly condition suitable for a seed bed." This permits proper drainage and circulation of air essential to bacterial activity and plant growth. Humus acts as a stabilizer. It makes the soil less sensitive to the ruinous coagulating effects of an excess of salts. Thus 15 to 20 per cent. of humus will almost obliterate the difference between a clay soil and a sandy soil. "Humic acid" is a mixture of allied substances rather than a definite chemical entity. Its calcium "salt" exercises a buffer action by combining with injurious acids and liberating the harmless, insoluble humic acid.

Many important properties of a soil, such as permeability, capillarity, absorption, moisture content, etc., are dependent not so much upon the chemical composition as upon the sizes of its constituent particles. In coarse sand, for example, the amount of water is greatest at the bottom and smallest at the top, whereas in fine clay the distribution is much more uniform. Clay consists of particles 0.002 mm. (2 microns) in diameter and smaller. Over about 18 per cent. clay gives a heavy soil, while under about 4 per cent. means a sandy soil of low water-retaining capacity.\* The effect of lime is so marked that a dressing of calcium carbonate will make an 18 per cent. clay soil act like a 12 to 14 per cent. soil, partly through the formation of calcium humate gel, which cements the finer particles into the desirable crumbly condition.

This also makes ploughing much easier; thus in the 1921-22 report of the Rothampsted Experiment Station it is stated that chalking heavy soil may reduce the power needed for ploughing by as much as 15 per cent.

Apart from the activity of bacteria, earth-worms and the like, the movement of substances in the soil is effected by diffusion and seepage of soil water. The forces acting may be divided into three groups, although, of course, there is no sharp line of demarcation between them: (1) Molecular forces of the order of 1,000 atmospheres; (2) capillary forces of the order of 3 to 4 atmospheres; (3) gravity. This corresponds roughly to the classification of soil water by Bouyoucos, as follows:

\* The application of colloidal clay or bentonite might be useful in such cases.

Gravitational water—"super-available."

Free water—very available.

Unfree water { capillary-absorbed—slightly available.  
 { combined { solid solution } —unavailable.  
                   { hydration }

The leaf system of plants is continually evaporating moisture, and the resulting hydration and osmotic "pull" is sufficient to raise a column of water even to the top of the tallest sequoia tree. It is registered as a root pull of about 7 to 8 atmospheres. The water evaporated by plants is continually replaced by rain, but in dry weather there results a struggle for water between the plant and the soil. The percentage of water left in the soil when the plant can no longer protect itself against desiccation by taking up soil moisture is called the *wilting coefficient*. Its value varies with different plants, and the great influence of particle size of the soil may be seen from the following table of the shrinking coefficient of Kubanka wheat (after Briggs & Shantz):

Soil	Wilting coefficient
Fine sand . . . . .	2.59
Fine sandy loam . . . . .	9.66
Clay loam . . . . .	16.3

An important factor in the struggle between the "root pull" of the plant and the "back pull" of the soil is the speed with which water can diffuse toward the roots. Cultivation of the soil above the roots exposes a greater soil surface to the air, and the resulting increased evaporation there causes increased upward and sidewise diffusion streams, which not only supply water to the roots at increased speed, but also carry the necessary plant food. As Bechhold observed



(Kolloid-Zeit. 27, 29, 1920), soluble salts follow diffusion streams. Thus if a piece of plaster of Paris be dipped in sulphate of copper solution and then dried, the copper will be found almost quantitatively in the exterior layers. W. Kraus (Kolloid-Zeit. 28, 161, 1921) showed that this "capillary phenomenon" of salt concentration is due to evaporation at the exposed surfaces. The plant is therefore enabled to make its necessary growth with less water, and as this growth generally is greatest in the wet season, *cultivation* or *tillage* by losing some water may actually enable the plant to enter the dry season with a reserve store of soil water in the soil, which in turn is made more rapidly available in the dry season by further cultivation. (J. Alexander, Science 1921). Cultivation also kills off competing weeds and aids soil bacteria which produce plant food in available form.

Contrary to popular idea, colloids do diffuse, albeit more slowly than substances molecularly dispersed, so that the roots may absorb soil colloids which diffuse toward them. While, of course, chemical reactions may go on in the soil, ionizable or hydrolyzable salts are apt to be split up and their fractions segregated by the action of selective adsorption and differential diffusion, giving results that cannot be simulated by simple aqueous solutions. Changes in effective reaction (hydrogen ion concentration) and other conditions affect the state of the soil colloids, and as their active free surface varies, they may hold or release adsorbed substances. Protectors also exert their influence.

In very permeable or sandy soils, especially if deficient in lime which holds the humus as a gel, the



alumina, iron and humus are apt to assume the sol form and be washed down by the rain to a lower stratum, where, by desiccation or electrolyte precipitation, they gradually form an insoluble rock-like layer known as a *pan*. Such a pan acts as an impermeable septum, shutting off the soil beneath from air and water, preventing diffusion between it and the top soil, and often causing swampy conditions.

A. S. Cushman [U. S. Dept. Agri., Bureau of Plant Industry, Bull. No. 104] showed that fine grinding of feldspar greatly increased the amount of potash available under the action of water. A coarse powder whose free surface was 43 sq. cm. per cc. yielded only 0.013 per cent., whereas a fine powder with a free surface of 501,468 sq. cm. per cc. yielded 0.873 per cent. of potash and soda, an increase of 6,700 per cent. Even then these fine particles averaged about 0.1 micron in diameter, which is about the upper limit of colloidal dimensions. In the soil they undergo further disintegration whereby still more of their potash becomes available. The availability of phosphate rock is greatly increased by fine grinding.

### Clays

The working properties of clays depend largely upon the size and the degree of dispersion and hydration of their constituent particles, and especially upon the proportion of colloidally dispersed particles. These factors are in turn influenced by the presence of protective colloids (e.g., humus), salts, and effective reaction ( $p_H$  value, hydrogen ion concentration). Thus the clay of Mesopotamia is baked into bricks by mere exposure to the sun, whereas straw was necessary

to make bricks out of the clay of Egypt (Exodus V). The straw may have been used as a fuel to burn the bricks, or else to improve the working quality of the clay, for recently patents have been taken out for "Egyptianizing" clay by the addition of tannin, extracts of straw and humus, etc. Glue and similar protective colloids deflocculate or "free out" clay and make it "cover" when used in paper-coating or kalso-mining.

*Bentonites* are fine clays resulting from the dusts deposited by ancient volcanos. Some varieties form suspensions that readily settle, but others are so highly colloidal that they swell in water just like glue or gelatin. These grades are used for "beauty-clays" and cataplasms, as well as for many technical purposes.

Clay in general is flocculated by acids and by acid or neutral salts. Small amounts of alkalies and of alkaline salts deflocculate it, but larger amounts cause flocculation. Clay slip, prepared with a little sodium hydroxide or carbonate, can be readily poured or cast, even though it contains less water than a stiff mass of clay and water without alkali. On adding a little acid to such fluidified clay slip, the mass immediately becomes so stiff that it will not fall from the inverted vessel.

Each clay as found in nature bears within itself much evidence of its past geological history: the chemical and mechanical processes of past ages; lixiviation by glacial or other waters; subsequent sedimentation in still lakes or flats, or coagulation by saline waters; leaching out of some salts or soluble products; infiltration of other salts and of organic extractives; the pressure of overlying strata; thermal changes due to

solar heat, volcanic action, or metamorphic movements of the earth's crust, which may also cause pressure.

Ultramicroscopic examination gives a very good insight into the nature, working properties and impurities of clays. [See J. Alexander: J. Am. Ceramic Soc. 3, 612 (1920).] Some idea can be formed of the relative percentage of colloidal and coarser particles, and the influence of protectors and coagulating salts traced. Fire clays show the combined effect of the infiltration of protective substances (from peat, lignite or coal deposits) and of salts or acids resulting from the diffusive decomposition of ferrous sulphate (oxidized pyrites). To work properly, clays must have the proper proportion of coarser, finer and colloidal particles, so that by washing and blending clays and working upon them with reagents more powerful than those ordinarily found in nature, we have a wide range of possibilities.

### Ceramics and Refractories

Following the principles above mentioned, the use of alkalis or alkaline salts to deflocculate clay and make a casting slip is general in the ceramic industry. Caustic soda and silicate of soda are largely used. If the clay mixture holds too much water, there will be excessive shrinkage upon drying; and if it is too hydrous, there will be too much shrinkage on firing. In either case the molded article will warp, and this must be prevented by proper selection, mixture and treatment of the clay used. To safeguard against warping, there is often added to the ceramic mixture some powdered burnt clay (broken pottery or grog).

When heated or "burned," clays become irreversibly dehydrated and harden into pottery, bricks, etc. Throughout the whole ceramic process, the pugging, blunging and aging of the clay, the molding and subsequent drying and burning, may be traced the influence of particle size and impurities, and their effects extend to the zone of actual fusion.

Fire clays have a preponderance of relatively large, consolidated or dehydrated particles, a result which may be brought about in nature by pressure, coagulating salts and a deficiency of organic deflocculators. They take up comparatively little water and therefore do not shrink much on drying. With clays exposed to high temperatures, the chemical composition, which influences the melting point, is vital.

There may be a "eutectic drop" in the case of the admixture of clays, just as there is with metallic alloys. Mixtures for Seger cones are based on the principles above referred to.

### Flotation

The importance of flotation processes is evident from the fact that in 1918 over 70,000,000 tons of ore were thus concentrated. The understanding of the principles of flotation will be simplified by bearing in mind that, notwithstanding the presence of many disturbing and variable factors, there are involved two main triphasic systems:

1. *Ore/water/oil*, from which the true ore (usually a sulphide) must emerge with a film of oil which enables it to be taken up by the air bubbles and thus floated off with the froth, while the gangue is wetted and flowed off at a lower level.

2. *Air/water/oil*, which yields the bubbles to float the oiled sulphide.



The oil clings to the sulphide because the surface tension oil/sulphide is less than the combined surface tensions ( $\sigma$ ) water/oil and water/sulphide.

$$\begin{aligned} \text{That is, } \sigma_{OS} &< \sigma_{WO} + \sigma_{WS}, \\ \text{or } \sigma_{WO} &> \sigma_{OS} - \sigma_{WS}. \end{aligned}$$

The oils or some of their constituents distribute themselves at the interface water/air, and thus form stable bubbles, because the surface tension water/air exceeds the combined surface tensions water/oil and air/oil.

That is,

$$\begin{array}{ccc} \sigma_{WA} & > & \sigma_{WO} + \sigma_{AO} \\ 75 & & 23 \qquad 33 \text{ (approximate values)} \end{array}$$

The air bubbles forming the froth thus have a more or less stable surface film which is miscible with, though not necessarily identical with, the oil film on the sulphide, for selective adsorption may effect some segregation of the oil constituents. However, the oiled ore particles act like oil; they distribute themselves at the interface water/air, are thus attached to the air bubbles and lifted to the upper froth layer unless they are too heavy or are knocked off.

Some of the complicating factors will now be considered.

*Water.*—Dissolved air aids bubble formation by reducing the internal pressure of the water; so that temperature of the water is important. Most crystalloids, especially acid electrolytes, act beneficially, for they are adsorbed by and coagulate the fine slimes, clay, etc., which then tend to repel the flotation oil. This recalls the old-fashioned household expedient for avoiding the taste of castor oil, by moistening the



mouth and throat with orange or lemon juice. Some electrolytes, especially small quantities of alkalies, are very detrimental, because by reducing the surface tension between the water and the oil and the sulphide and the gangue, they tend to emulsify the oil, wet the sulphide and deflocculate the slimes. Humic substances, especially in the presence of alkali, and protective colloids in general, act in like manner; thus glue is very injurious. Colloidal clay or very fine gangue may have a similar action, for they may act as emulsifiers—"fat" clays emulsify oils, tars and asphalts.

*Ore.*—Some ores yield soluble substances which exert an effect, but as a rule the fineness of grinding is the most important factor. While the gangue must be fine enough to flow off readily under the conditions of operation, it should not be so fine as to cause the undesirable emulsification above referred to. The sulphide particles, if too large, are not lifted or are readily knocked off; if too small the bubble surface is covered by too small a weight of ore, and there is great loss in efficiency. The tiny ore particles should make a substantial armadillo-like covering about the air bubbles, which aids in the stabilization of the bubbles.

*Oil.*—Many substances used in flotation—e.g., cresols—are not oils at all, and many substitutes for oil have been patented. The rapid development of the flotation industry created a sudden demand for materials like pine oil which previously had a limited demand, and markets were thus turned topsy-turvy. Mixtures of substances may be used as "oil," for the foam-producing and the sulphide-oiling factors are not necessarily identical. The percentage of oil is

also important from an operative as well as from a patent standpoint.

The whole question of flotation demands intensive study and experience. Thus Callow estimates that with four different oils, three different oil percentages, two pulp densities and two temperature changes, there are possible about 60,000 different combinations of conditions.

## CHAPTER 9

### PRACTICAL APPLICATIONS (Continued)

#### DYEING

Four principal theories of dyeing have held the field: (1) The mechanical or physical theory; (2) the chemical theory; (3) the colloid-diffusion and adsorption theory; (4) the electrical theory. A complete historical review of these theories, with bibliography, is given by P. E. King in the First Report on Colloid Chemistry and Its Industrial Applications, published by the British Assoc. for the Adv. of Science, London, 1917. In the Second Report, London, 1918, W. Harrison discusses at some length the colloid chemical nature of the various textile fibers, as well as the electrical theory of dyeing.

There are many different types of dyes and thousands of different individual dyestuffs, and the various fibers, tissues, etc. (cotton, silk, wool, linen, jute, straw, paper, wood) all react characteristically. The phenomena of dyeing are, therefore, very numerous and complicated. In essence the conflicting theories are not so divergent as might be imagined; they differ mainly as to the classification of the attractive force between substrate and dye.

Since all forces of the nature involved are ultimately due to electro-magnetic fields of the atoms involved (or of their electrons), the attraction is essentially electrical or chemical; but since this attraction is exhibited only when the dye and substrate expose sufficient active free surface, the operation is "physical" or "colloidal." Although forces closely allied to those

of primary valency are involved, the compounds formed do not in general possess that preciseness connoted by the present meaning of the expression "chemical compound."

In some cases the colloid fiber adsorbs the dye, as with basic colors which dye silk and wool directly. In other cases there is necessary a *mordant*, which is first adsorbed and then fixes the color; e.g., for some dyes cotton must first be mordanted with an insoluble colloid precipitate formed *in situ* by tannin and tartar emetic. Certain dyes of opposite charge may mutually precipitate each other, and thus serve as mordants for each other; e.g., methylene blue and dianil blue 2 R; patent blue V and magenta. But a large excess of either dye may serve as a colloidal protector and either prevent the precipitate or make it colloidal. Grüber's stains owe their peculiar properties mainly to colloidal impurities (dextrin, etc.), so that the same dyes when spectroscopically pure, work differently.

Ultramicroscopic examination reveals the fact that many dyes are colloidal in solution, and the selective coloring of fibers, tissues, cells, nuclei, etc., probably represent the selective adsorption or precipitation of one colloid by another, a view sustained by the ultramicroscope researches of N. Gaidukov. Some dyes can be extracted from the dyed fiber by alcohols, which would hardly be the case if a true chemical compound were formed. There is an optimum degree of dispersion for each dye [zone of maximum colloidality (see p. 17)]. This is shown by the work of R. Auerbach [Kolloid Zeit. 34, 109, (1924)] which indicates that if too coarse the dye lacks diffusive power; and if too fine it passes out of the fiber once more.

(J. Alexander, Am. Chem. Soc. Washington Meeting, 1924.) Temperature, and the addition of salts ( $\text{Na}_2\text{SO}_4$ ), acids, colloidal protectors (boiled off silk liquor) and the like are used by practical dyers to control the degree of dispersion.

Colloid chemistry also throws much light upon many obscure points in the practical art of dyeing. It is possible to obtain much more level colors in old dye liquors than in fresh ones, and here it seems that colloiddally dissolved substances are responsible, exercising a restraining action upon the absorption of the color. The addition of Glaubers' salt facilitates level dyeing, probably by its action as an electrolyte, producing a partial coagulation of the dyestuff, so that the particles of the latter, thereby made larger, are absorbed more slowly and evenly.

Congo red when dyed on silk or wool changes only in shade if the fiber is dipped in dilute sulfuric acid, whereas when dyed on cotton it turns blue in like circumstances. Upon following ultramicroscopically the changes produced in colloidal aqueous solutions of benzopurpurin, J. Alexander found [J. Soc. Chem. Ind. 1911, Vol. 30, No. 9] that the color change was accompanied by an aggregation of the dye ultramicros. If a protective colloid such as glue was added to the dye solution before the addition of acid, the dye ultramicros did not aggregate, and the color change could thus be modified or prevented. It seems, then, that silk and wool exercise a greater protective action on the adsorbed dye than does cotton, which harmonizes with the fact that proteins are in general better protectors than carbohydrates. This is also evidence against the chemical theory of dyeing in this case.



### Shower-proofing Fabrics

If textile fabrics and the like are coated with a surface film of wax, aluminium stearate and so on, they are not wet by an ordinary shower, whose drops roll off "like water off a duck's back." With an untreated fabric the attraction between the fabric and water bursts the surface skin of air on the fabric and the surface film of the raindrop, which then spreads itself out on the fabric and is absorbed into its pores.

Remembering that as the attraction between surfaces increases the surface tension between them decreases,\* this means that wetting occurs when the surface tension ( $\sigma$ ) water/fabric is less than the combined surface tension water/air and air/fabric. That is,

$$\begin{aligned}\sigma_{WF} &< \sigma_{WA} + \sigma_{AF}, \dagger \\ \text{or } \sigma_{WA} &> \sigma_{WF} - \sigma_{AF}.\end{aligned}$$

Since surface tension is only "skin deep," the surface tension water/fabric really becomes that of water/wax and is greatly increased. Therefore,

$$\begin{aligned}\sigma_{WF} &> \sigma_{WA} + \sigma_{AF}, \\ \text{or } \sigma_{WA} &< \sigma_{WF} - \sigma_{AF},\end{aligned}$$

the water is repelled and no wetting occurs.

### Nitrocellulose and Its Products

When cellulose (cotton, purified paper pulp) is soaked in a mixture of nitric and sulphuric acid, it takes up from 10 to 13 per cent. of nitrogen, depending upon the purity and moisture content of the cellulose, the exact composition of the acid bath and the time and

\* In fact, when the surface tension in a two-phase system becomes zero, solution or colloidal dispersion may occur.

† W = water, F = fabric, A = air,  $\sigma$  = surface tension.

temperature of nitration. The formation of a series of cellulose nitrates is generally assumed, although A. Müller suggested the existence of adsorption compounds. In any event the acid fixation curve is continuous, notwithstanding numerous attempts to separate out definite nitrates. Cellulose has a structure, the interior of a cotton fiber being less dense than the exterior, and since the nitration starts at the surfaces and leaves them comparatively undisturbed, its course will evidently be dependent upon the amount of free surface exposed. It has been found that by intensive grinding cellulose yields a colloidal solution in water.

The colloidal solutions that result from dissolving cellulose nitrate in various solvents or mixtures, are widely used as varnishes and lacquers to coat patent and artificial leather, metals, etc. Their degree of dispersion and therefore their viscosity is dependent upon the nature of the solvent, whose action may depend upon small percentages of substances which exercise a peptizing action. Thus old patents claimed that nitrocellulose dissolved in wood alcohol, because the "wood spirit" of those days contained ketones, small quantities of which are essential; for the nitrate is insoluble in pure methyl alcohol. According to F. Sproxton [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], if water be added in gradually increasing quantities to an acetone solution of cellulose nitrate, keeping the percentage of the solute constant, the viscosity rises to a maximum (both absolutely and relatively to the viscosity of the solvent) and then falls until it is practically the same as that of the solvent. This seems to be another illustration of the zone of maximum degree of colloidality [see J. Alex-

ander, J. Am. Chem. Soc. 43, 434, 1921], for the Tyndall effect becomes marked close to the position of maximum viscosity.

### Celluloid

This is a transparent gel formed when nitrocellulose is kneaded with alcohol and camphor. In the subsequent sheeting, pressing and molding operations it undergoes a slow syneresis due to the loss of the alcohol and some of the camphor. Schüpphaus [Thorpe's Dict. Appl. Chem., vol. 1] thinks that there is some kind of chemical combination between the camphor and the nitrocellulose because the heat of combustion of the two ingredients is greater than that of celluloid itself. This, however, is no criterion, for as Prange has shown [Recueil des Trav. Chim. des Pays Bas, 9, 121 (1890)] colloids may set free heat if their particles aggregate, and heat is liberated when nitrocellulose and camphor are mixed. Furthermore, according to Sproxton, the optical rotation of a dilute acetone solution of celluloid equals the sum of the rotations of its two ingredients.

The view of Dubosc [Le Caoutchouc et la Gutta Percha, 1919, p. 9803] that celluloid is a camphorgel (nitrocellulose dispersed in camphor) seems well warranted by the facts. Its plasticity on heating to 80 deg. C. is attributed to the fusion of the dispersion medium, camphor, which diminishes the internal friction. The fact that camphor constitutes only about one-third the bulk of the celluloid does not militate against this view (as Sproxton suggests), for S. U. Pickering was able to emulsify 99 per cent. of petroleum oil in 1 per cent. of soap solution, obtaining an almost solid emulsion.

### Explosives

The modern propellant explosives consist of nitrocellulose colloided with ether/alcohol, nitroglycerin, etc. The rate of burning of the grain is intimately connected with the external and internal surfaces of the explosive, the former being controlled by the size, shape and perforations of the pieces, and the latter by careful regulation of the manufacturing process. Variations in the original cellulose, the process of manufacture and the presence of traces of impurities may materially alter the stability and ballistic properties of the product as well as the viscosity of its solutions.

Blasting gelatin is a colloidal gel of 7 to 8 per cent. nitrocellulose with nitroglycerine, the former probably being the dispersed phase. There is evidently an optimum internal structure for this colloid, since its tendency to become insensitive on aging is a bane of the manufacturer. The use of a protective colloid seems indicated here; it will also probably tend to prevent the exudation of the dangerous nitroglycerine, which is especially apt to occur on freezing, and constitutes a serious danger on thawing or subsequent handling.

### Paints, Pigments, Varnishes

When linseed oil, China wood oil, etc., begin to polymerize upon boiling, they form *isocolloids*, that is, a dispersion of the polymerized in the unpolymerized oil. Highly boiled China wood oil sets to a gel. The various varnish gums go into colloidal dispersion, and it seems not improbable that they may act as protectors to the boiled oil, keeping it from gelatinizing. What is known as the "break" in boiled oils is the



coagulum resulting from the albumin, etc., which must be filtered or settled out.

*Varnishes* must possess a very fine internal structure when dry, for they permit the swelling of gelatin protected by the varnish film. In most cases the internal spaces permit the formation of a cloudy dispersion or emulsion of water in the film, but with the most highly protective varnishes they are so fine that although as much as 5 per cent. of water be taken up, the film remains clear. The impermeability of the varnish film to most salts indicates the fineness of the pores; but since water absorption increases with diminishing salt concentration, it would seem that the salt by adsorption or swelling causes a diminution of the size of the pores. Normal solutions of  $\text{NaCl}$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  prevent the ordinary varnish film from turning white, and greatly diminishes the amount of water passing through.

*Shellac* contains about 4 per cent. of wax, which goes into colloidal dispersion in most solvents. In solutions over about  $3\frac{1}{2}$  lbs. per gallon the wax does not readily settle out, but weaker solutions show a separation of wax-free "*French varnish*" or clear shellac solution.

*Pigments* vary greatly in their degree of dispersion which vitally controls their opacity, surface covering power, and oil-absorbing capacity. Because of the importance of the physical condition, mere chemical analysis is quite insufficient to rate pigments. The most finely subdivided oxide of zinc commands the highest price, chromates of lead vary in color from lemon yellow to orange and Prussian blues vary in shades as their particle size changes. The difference



between blanc fixe (precipitated  $\text{BaSO}_4$ ) and ground barytes is enormous. Too great a degree of dispersion is harmful, for there is an optimum degree of dispersion on either side of which desirable properties begin to diminish. The cross-precipitation of BaS by  $\text{ZnSO}_4$  yields a product so highly colloidal that it is furnace-dried and powdered to produce a more compact lithopone. The fact that a mixture of blanc fixe and zinc sulphide does not give the same degree of opacity as lithopone indicates that in the latter there is a close adsorption. Generally in making precipitated colors or color bases the degree of dispersion is controlled by temperature, colloidal or other protectors (or even coagulants), and the concentrations and speed of mixing of the reacting solutions. [See H. A. Gardner, J. Ind. Eng. Chem. 8, 794 (1916).]

While *paints* are essentially mixtures of pigments, drying oils, and solvents, the presence of small amounts of other substances may be highly desirable. Thus E. G. Acheson [J. Soc. Chem. Ind. 30, 1426 (1921)] states that the addition of a minute amount of tannic acid causes a pigment to deflocculate readily on grinding in oil, and the use of about 2 per cent. of water emulsified by such a substance as silicate of soda has long been common in mixed paints to prevent hardening or settling in the can. Ware and Christman [J. Ind. Eng. Chem. 8, 879 (1916)] found that the addition of aluminium palmitate or oleate to paints helps this condition; these non-aqueous protective colloids aid in keeping the pigment in suspension, partly because they increase the viscosity of the oil. These authors also investigated the "livering," puttying, and skinning of mixed paints. Livering is attrib-

uted mainly to the formation of a zinc soap gel, the formation of which is aided by the presence of zinc resinate (formed from rosin used in the paint) and acid pigments.

An interesting application of colloid chemistry was made by Wheeler P. Davey, of the General Electric Co., who made a "*water japan*" by emulsifying japan base (mainly a solution of asphalt in a drying oil) in water containing ammonia and a protective colloid. Besides being cheaper and less hazardous than the ordinary japan made with petroleum solvents, the water japan is much less viscous and small pieces of metal may be coated by first heating them and dipping them *en masse* in baskets into the emulsion. As the japanned particles are negatively charged, they may also be deposited on the metal by making it the anode in an electric circuit. In both cases the japan base attached to the metal is free from solvent, and is baked as usual; "secondary drip" and scars due to mutual contact between the metal pieces are largely avoided by the wide latitude permitted in the composition of the base, for these changes do not seriously affect the viscosity of the emulsion.

### Emulsions

An emulsion is a fine dispersion of one liquid in another. Since the interfacial tension between benzol and water is very high (about 35 dynes per sq. cm.), if benzol and water are agitated together, the benzol droplets tend quickly to unite, and the liquids separate into two layers. If there is a very small percentage of benzol, this process takes quite a while, especially if the benzol droplets are very small; so that the dilute emulsion has a limited life.

If however the aqueous phase consists of sodium oleate solution 0.01 normal or stronger, the interfacial tension is reduced to about two dynes per sq. cm., and vigorous agitation gives a stable emulsion. As J. Willard Gibbs showed, the sodium oleate, tending to reduce the interfacial tension, accumulates at the interface, and practically surrounds the emulsified droplets with a coherent film.

Taking Harkin's view of oriented adsorption, the hydrocarbon end of soap will direct itself toward the oily liquid, while the metallic end will point toward the aqueous phase. If, now, the fatty ends of the molecule can pack together closer than do the metallic ends, the interfacial film bends *toward the oil*, and we have an emulsion of oil in water. This is the case with sodium, potassium and cæsium soaps; and indeed Finkle, Draper and Hildebrand found that the size of the oil drops in emulsions, made with soaps of these alkali metals, varied as this theory demands [J. Am. Chem. Soc., 45, 2780 (1923)].

If, however, a soap of a bi- or trivalent metal (calcium, aluminium, magnesium, lead or the like) be used, which has several hydrocarbon chains attached, then the interfacial film bends *towards the water*, and we have an emulsion of water in oil. Thus are explained the observations of G. H. A. Clowes on the reversal or inversion of emulsions and the variation in the number of drops when oil is dripped into various solutions from a staglomometer (drop measurer).

W. D. Harkins and his collaborators have developed the principles governing this oriented wedge theory of emulsions and the inversion of emulsions [see J. Am. Chem. Soc. 39, 587 and 592-4 (1917); also "Science," May 23, 1924].

The preparation of stable emulsions is of importance in pharmacy (cod-liver oil, etc.) and cookery (mayonnaise, hollandaise sauce, etc.); and the biological importance (myelins, nerve tissue, fat depots, etc.) is obvious.

The "breaking" of undesirable emulsions (de-emulsification) is also of considerable practical importance. Thus many petroleum products contain large amounts of emulsified water which must be removed. The basic method of F. H. Cottrell [U. S. P. 287, 115 (1911)] makes use of high tension electric current [for details see *J. Ind. Eng. Chem.* 13, 1016 (1921)]. Besides this filtration, chemical, and centrifugal methods are used to break the interfacial films and permit the droplets to coalesce. In some cases even as little as 0.001 per cent. of a protective colloid will do this, by coagulating the emulsostatic film. Freezing does the same thing in other instances. (For further details see W. Clayton's book on "Emulsions and Emulsification," Blakiston, 1923.)

## CHAPTER 10

### PRACTICAL APPLICATIONS (Continued)

#### SOAPS

The orthodox view that soaps are simply alkali salts of fatty acids was considerably shaken when Lewkowitsch [J. Soc. Chem. Ind. 1907, 26, 590], after epitomizing the views of Merklen, said:

But whatever may be the outcome of renewed experiments, Merklen's views cannot fail to stimulate further research into the composition of soap, and thus help raise the industry of soap-making, which has too long been looked upon as a mere art, to the rank of a scientifically well-founded industry, the operations of which are governed by the laws of mass action, the phase rule, and the modern chemistry of colloids.

Merklen's views which aroused this comment are that commercial soap is a product of essentially variable composition which depends on (1) the nature of the fatty acids, (2) the composition of the "nigre" (in the case of settled soaps), (3) the temperature at which the boiling is conducted. It behaves like a colloid, and should not be regarded as a compound of fatty acids having chemically combined a definite amount of water, but is rather an "adsorption product" whose composition depends upon the environment in which the fatty acid salts find themselves at the moment of the finishing operation.

According to J. W. McBain [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], homogeneous solutions of soap are rarely met with during the process of manufacture, since their viscosity would be pro-



hibitively great, and must be held in check by the addition of caustic soda, salt, or other electrolytes, to bring the soap into a gel or even into coagulated form (soap curd). The soap is usually in the form of a dispersion of two soap solutions, soap-in-water, and water-in-soap, and may exist in the form sol/sol, sol/gel, or sol/curded-gel.

Most commercial soaps are of the sol/curded-gel type, but soft soaps may be of the sol/gel type. McBain regards soaps as colloidal electrolytes, that is, as salts in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle which exhibits a high conductivity.

Martin H. Fischer ["Soaps and Proteins"] has shown that the hydration capacity of soaps varies greatly with change in the fatty acid, and the base. Some soaps hold enormous amounts of water, while others hold very little, so that if the amount of water present exceeds the hydration capacity of the soap, free water separates or may remain emulsified (see p. 19).

Most soaps form crystalloidal solutions in alcohol, which ultramicroscopically are quite clear; but if a droplet of tincture of green soap, for example, be allowed to diffuse into a clear field of pure water held between a slide and cover glass in a dark-field condenser, the soap practically explodes into numberless actively moving ultramicros. The colloidal nature of aqueous soap solutions is further indicated by their turbidity, viscosity, and gelatinization.

The *detergent action* of soap is due to its ability as a colloid to produce deflocculation. Hillyer [J. Am. Chem. Soc. 1903, 25, 511, 1256] showed that this action is not due to alkali freed by hydrolysis, and that

alkali itself does not wet oily matter. But all "dirt" is not oily, and W. Spring [Kolloid Zeit. 1909, 4, 161; 6, 11, 104, 164] in experiments with purified lamp-black, iron oxide, alumina and silica, showed that soap makes such particles less adherent to the fabric, and to each other. The attraction of both fabric and "dirt" for soap exceeds the attraction of the fabric for "dirt" and of "dirt" particles for each other. In order that the soap may be adsorbed at the interfaces involved, it must be in colloidal dispersion, which requires hot water in the case of many soaps.

The practical working properties of various commercial soaps depend mainly upon the nature of the fatty acids in them. Thus sodium oleate is much more readily dispersible in water to colloidal dimensions than is sodium stearate, and even small amounts of oleate materially assist the higher fatty acid soaps to dissolve. In fact mixtures of fats or fatty acids show a "eutectic drop" in melting point, just as do alloys. From the oriented wedge theory of emulsions (see p. 96) it is evident that in an emulsion of oil in water, potassium soaps, having larger molecules (K) turned to the water phase than the sodium soaps (Na), tend to make a foam with smaller bubbles, which is therefore more stable. For this reason shaving soaps consist largely of potassium soaps.

H. Jackson [Cantor Lecture, J. Soc. Arts, 1908, 55, 1101] examined microscopically the supernatant fluid resulting from washing a piece of dirty cloth with soap and water, and found in it countless particles in a state of oscillatory motion ("*pedesis*"). This is really *Brownian motion*, first noted by the English botanist Robert Brown in particles approaching the

limit of microscopic resolvability. The ultramicroscope shows it to be largely due to bombardment of these larger particles by the still smaller and more actively moving colloidal particles, which in turn are activated by the motion of still smaller particles (water molecules), and so on. When an individual fiber was bathed in soap solution, the dirt particles gradually loosened and began to oscillate. Upon substituting salt solution for the soap, the particles flocculated and the motion ceased. An ultramicroscopic examination of the detergent action of soap is very interesting.

*Transparent soaps* are made by keeping the dispersion of the particles of the finished soap well toward the lower limit of colloidal dimensions. Among the factors that produce this effect are (1) the selection of the fatty acids; (2) quick chilling; (3) protective colloids; (4) the addition of alcohol, glycerol, sugar and the like, which tend to dissolve the soap crystalloidally. Frequently some of the fatty acid salts crystallize out in the clear matrix, marring the commercial appearance of the soap, and these crystals exhibit the dendritic or ramifying tendency common when crystallization occurs in the presence of colloids. W. D. Richardson [J. Am. Chem. Soc. 30, 1414] found that the fatty acids separated from the crystals had a higher melting point than those separated from the clear matrix.

To demonstrate the effect of the speed of chilling on particle size, J. Alexander melted a piece of commercial transparent soap and cast it into two cups, one of which was instantly chilled with ice, while the other was allowed to cool slowly while immersed in hot water. The quickly chilled piece was transparent and upon

ultramicroscopic examination showed much smaller ultramicros than the slowly cooled piece, which was opaque. After several months standing the quickly chilled soap still appeared clear, whereas the other had large opaque spots. Upon ultramicroscopic examination the transparent piece appeared as before, but the slowly cooled piece showed perfectly resolvable crystals in a clear matrix.

### Lubrication

The automobile has brought such an increase in the consumption of petroleum that a material curtailment in supply, if not actual exhaustion, lurks in the not far distant future. But we may look with confidence to colloid chemistry to supply the lubricants of that day.

The principle involved in lubrication is the maintenance, on each of the surfaces in contact, of an adsorbed layer of an easily deformable substance (usually a fluid) so that the surfaces can not come into actual contact, or "seize." Since the attractive forces at surfaces depend on their residual electrical fields, lubrication is affected by the chemical and physical nature of the surfaces as well as by that of the lubricant. Good lubricants are so strongly absorbed that great pressure and speed are necessary to tear them loose.

W. B. Hardy [J. Soc. Chem. Ind. 1919, 38, 7 T] made some illuminating experiments with glass, which absorbs from the atmosphere rather more of its impurities than of the elementary gases, yielding a film about 1 millimicron ( $1 \times 10^{-7}$  cm.) thick, that Lord Rayleigh termed "grease" because it has the properties of an oil. This "grease" tends to make pipettes



deliver inaccurately, so analytical chemists remove the absorbed layer by oxidation with bichromate and sulphuric acid.

For the same reason new or raw glass surfaces have mechanical properties different from those of a satisfied or neutral surface. Thus a finger bowl or tumbler does not give a musical note when rubbed with the wetted finger, unless the "grease" film is removed by vigorous rubbing with the finger tips until a peculiar clinging feeling is felt, due to "seizing" between finger and glass.

Experiments with cleaned glass surfaces have shown that water, ether, alcohol, benzene and strong ammonia do not prevent "seizing" even if the surface be flooded with them. A thin film of glycerin did not lubricate, but flooding the glass surfaces reduced the tangential force required to move them from 55 grams to 9 grams. Most acids, for example, sulphuric, acetic, oleic, lubricate better in thick layers.

Because animal oils, such as sperm or lard oil, are more highly adsorbed by metal surfaces than are petroleum oils, they have long been blended with the latter in considerable quantity to improve the lubricating value. It has been found, however, that such additions owe their value largely to the free fatty acids present which are highly adsorbed, and Southcombe and Wells patented the addition of about 1 per cent. of such acid to mineral oils, thereby effecting a great saving, by avoiding the cost of the blending oils.

Most lubricating greases are colloidal oil/water emulsions stabilized with sodium or calcium soaps. The so-called "cutting oils" which form stable emulsions with water are made by mixing petroleum with



water-soluble protective oils like turkey-red (sulphonated) oil. The thrust boxes of steamers which absorb the tremendous pressure of the propellers are lubricated and cooled by circulating an emulsion of oil and water.

The viscosity of oils, which is an important factor in lubrication, seems to depend to a considerable extent on the degree of molecular aggregation. Thus Dunstan and Thole (J. Inst. Petrol. Tech. 1918, 4, 191) found that mineral and fatty oils show an exceedingly fine heterogeneity in the ultramicroscope which they attribute to iso-colloidism.

### Coal

In recent years the complicated substructure of coal has been given much attention. In banded bituminous coal the following constituents are recognized (M. C. Stopes, Proc. Roy. Soc. B, 90, 470 (1919):

*vitrain*, brilliant, with conchoidal fracture.

*durain*, dull, hard coal.

*clarain*, bright coal.

*fusain* ("mother of coal" or "mineral charcoal"), is the most friable portion whose fineness controls the speed with which combustion spreads in the mass. When very fine it absorbs oxygen with avidity, and this may be a factor in *spontaneous combustion*.

Stopes and Wheeler (Monograph on Constitution of Coal, Brit. Dept. Sci. Ind. Res. 1918) define ordinary coal as a compact, stratified mass of mummified plants (which have suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter. Although coal retains to

some extent the structure and general chemical nature of the original plants, the presence in peat of Dopplerite (a dark, apparently structureless jelly) indicates that part of the coal was probably in this state, which may account for some of the adsorbed substances found in coal.

Reinhardt Thiessen (U. S. Bureau of Mines, Bull. 117; Journ. of Geology, 28, 185-208, 1920), divides the main constituents of coal into (1) *bright* or *glanz* coal, (*antharyxalon*) compact, pitchy jet-black, and of conchoidal fracture, formed from undisintegrated trunks and large limbs and retaining the original woody structure, and (2) *dull* or *mat* coal, less compact, dull grayish, and showing an irregular fracture; consisting of numerous small layers or chips of anthraxylon embedded in a dull matrix, the *attritus*, which is derived from assorted vegetable residues.

In the very nature of things, classifications of coal constituents must be rather arbitrary, but it is evident that the sub-microscopic structure of coal has much to do with its practical working properties.

### “ Colloidal ” Fuel

“Colloidal” fuel consists of finely powdered coal, cheap tars and the like, dispersed in mineral oil and stabilized by a protective colloid or “fixateur” such as lime soaps or resinates, so that it may be stored, piped, atomized and burned practically like oil itself. As this new composite fuel will at one stroke relieve the drain on the earth’s rapidly diminishing stores of petroleum, and lead, as well, to the utilization of coal waste (culm, screenings), inferior fuels (peat, lignite), and even cellulose waste (slabs, sawdust),

it may become a material factor in the conservation of our natural resources.

Coal or other combustible solid is prepared for dispersion by being pulverized so that about 95 per cent. passes through a 100-mesh screen, and 85 per cent. through a 200-mesh screen. This means, of course, that the bulk of the weight is in particles hundreds and thousands of times larger than colloidal dimensions. But the violent motion of colloidal particles aids in maintaining the Brownian motion of larger particles which helps to keep them afloat. A fluid fuel may be made containing as much as 40 per cent. by weight of powdered coal, and mobile pastes containing up to about 75 per cent. Mobile gels may be made from either liquid or paste.

Ordinarily between 0.5 and 1.5 per cent. of rosin or a saponifiable oil is used, and 0.1 per cent. exercises a noticeable effect. The amount is determined by the nature of the mixture and the degrees of permanence desired. The bulk of the particles does not begin to settle until the period of "life" has passed, the colloidal fuel having a limited "life" which may be regulated to meet requirements—days for power plants, weeks and months for central storage stations and ocean-going vessels. Heat and agitation revivify the liquid fuel; the paste form may be kept for years.

"Colloidal" fuel is heavier than oil or water and saves storage space by compressing a maximum thermal value per unit of space. It may be stored under water to avoid evaporation, deterioration and fire risk. When sprayed into the hot fire-box, its oil-soaked solid particles are still further atomized by

the sudden gasification of their imbibed oil. It possesses the advantages of fuel oil over coal in absence of smoke, dust and ash, practical elimination of labor in firing and filling storage space, thus saving time in "coaling" and in raising steam. The fire is likewise subject to instant control, and in naval operations a smoke screen may be readily produced by over-firing.

Another well-known colloidal fuel is "solidified alcohol," an alcogel usually stabilized by an alcohol-soluble protector. Thus the late Prof. Charles Baskerville found that certain percentages of calcium acetate yielded with alcohol an unstable gel, which is stabilized by stearic acid.

### Petroleum

Colloidal phenomena are very marked in mineral oils. Many oils contain colloiddally dispersed water which is difficult to remove. Cottrell devised a method of removing it with high tension current. He also was able to send viscous asphaltic oils through pipe-lines by emulsifying in them a certain percentage of water. The solid constituents of petroleum, especially the waxes, are largely in colloidal dispersion, some apparently serving as protectors to the others.\* This phenomenon is common, being found in alloys, glasses, mixtures of waxes, fatty acids, etc. When the kerosene and lower boiling fractions are removed from such oils, the solids, on chilling with ice, often assume the form of a gel which may be broken up by stirring or shaking, somewhat like agar gel.

*Bloom* in oil seems to be in part caused by some colloidal constituent.

\* See e. g. H. V. Dodd, Chem. Met. Eng., 23, 249, (1923).



As Brooks and Humphrey have shown [J. Am. Chem. Soc. 40, 882 (1920)], the "acid tar" which forms when petroleum is refined with sulphuric acid represents the coagulation of a previously existing colloidal dispersion of asphaltic bodies and the like, and not a polymerization product of olefines. Even 100 per cent. acid at 15 deg. C. does not produce tars from pure olefines. In some cases impurities may be centrifuged out, but they are largely removed by absorption with fuller's earth, floridin, bentonite, bauxite or other adsorbents. Patrick's colloidal silica gel and activated carbons are now used to adsorb the petroleum dispersed in natural gas, which yields millions of gallons annually of the high-grade "casing head" gasoline.

Great care must be used in drilling oil wells, for if the oil sands below ground get *wet* with water, surface tension makes the sand repel the oil, which is then unable to diffuse toward the well-pipe. Once the sands are *oiled*, however, then water cannot wet them.

In oil shale the oil is so finely dispersed that it cannot be removed by mere pressure. Distillation is resorted to, though doubtful claims are made that grinding in the colloid mill will effect a separation.

### Asphalt

Although most of the mineral matter in asphalt exceeds colloidal dimensions, as Clifford Richardson has shown, the great extension of free surface caused by its presence adds considerably to the viscosity, strength and wearing properties of the asphalt. The minerals here function somewhat like the fillers in putties and lutes. Natural asphalts may be improved by the addition of colloidal clays.



L. Kirschbraun has patented a colloidal aqueous dispersion of asphalt, pitch, etc., which, when mixed with paper stock in the beater or on the way to the paper machine, may be flocculated out with alum or alum and sodium silicate, giving a highly waterproof and moisture-resisting paper. This asphalt dispersion is not sticky or adhesive under the conditions of pressure, etc., in the paper machine.

Among the many uses to which such emulsions are being put are protecting structural steel, patching roofs and highways, making waterproof cork insulation, pipe coverings, paints, building and roofing papers, auto body parts, and especially making a large variety of moisture and waterproof containers and wrappers for foods, tobacco, etc.

### **“ Fire-Foam ”**

“Fire-Foam” is a carbon dioxide froth made by mixing solutions of sodium bicarbonate and alum. A protective colloid such as liquorice, glue, dextrin, or saponin, is added to stabilize the foam and keep the bubbles in finely dispersed form.

### **Insecticides**

Petroleum oils are readily emulsified in water for killing San Jose scale and similar parasites, by the addition to them of sulphonated oils. Sulphur, Bordeaux mixture and the like are maintained in fine dispersion by colloidal protectors, as are also such poisons as lead arsenate. Minute quantities of poisons are sufficient to kill insects and it is wasteful to supply more than the necessary dose. The colloidal poison is less apt to be noticed and rejected by the insect and clings better to the plant, and goes much further.

Even allowing for the necessity of a rather promiscuous distribution of insecticides, in general the use of coarse particles means that the factor of safety is exceeded hundreds if not thousands of times; and this means enormous economic loss.

The electric charge of the dispersed insecticide is of importance. Since the leaves of plants are mostly negatively charged, positively charged colloids tend to cling closely to them, as has been pointed out by Dr. William Moore.

## CHAPTER 11

### PRACTICAL APPLICATIONS (Continued)

#### FILTRATION

To secure commercially successful filtration, a filtering medium or septum must be used, which, under the application of a practicable pressure, will permit the fluid to pass and still hold back the solids. The pores of the filter may initially be small enough, or they may become so by the deposit of some of the precipitate itself or of some added substance, such as paper pulp, shredded asbestos (Gooch crucible), or the like. Exceedingly dense filters may require the application of high pressure to force the fluid through, and such high-pressure filters were termed by Bechhold *ultrafilters* because they could be made to hold back ultramicroscopic particles. Bechhold ("Colloids in Biology and Medicine," translated by Dr. J. G. M. Bullowa) used gelatin jellies hardened in ice-cold formaldehyde, or a glacial acetic acid solution of collodion coagulated in water. These septa were supported on fine-meshed wire cloth to withstand the high pressure used.

Zsigmondy has recently prepared *ultrafilters for analytical use*, which permit the rapid and successful filtration of troublesome precipitates [see Zsigmondy and Jander, Zeit. anal. Chem. 58, 241 (1919)].

The so-called *stream-line filter* of Hele-Shaw consists of paper sheets tightly pressed together, with holes bored through the pack at right angles to the surface. Liquids are forced under pressure into one set of holes and pass between the sheets to the adjoining set. By

sufficient compression of the sheets, even Prussian blue may be filtered out of solution.

Anything that favors deflocculation of a precipitate or the formation of a fine or colloidal precipitate, such as protective colloids, dilute alkalis, and so on, works against clear filtration. Thus Zsigmondy found that a gold hydrosol, whose particles were 20 to 30 millimicrons, passed freely through Pukall and Maassen filters if egg albumen was present. In the absence of the protective albumen, the colloidal gold was absorbed by the filters, gradually clogging their pores until the filtrate, at first red, became colorless.

In technical practice, wherever possible, a coagulated precipitate is formed whose large particles are held back with comparative ease. Therefore, glucose liquors, for example, must be acid to filter well. Where protective colloids interfere with filtration, their protective action may be destroyed by coagulation, hydrolysis and the like.

### Sewage Disposal

Sewage usually contains considerable amounts of deflocculating substances, such as soap, organic matter and the like, which tend to keep it full of colloiddally dispersed particles. The successful treatment of sewage, backwaters, and trade effluents involves the separation from them of these colloids by coagulation, adsorption, filtration, or destruction (usually by bacteria in the septic tank). The old "ABC" method depended on the use of alum, blood, and clay (whence the name) to make a coagulum that would carry down suspended matter. Ferrous sulphate and lime (yielding a coagulum of ferric hydroxide) and alum are

also used as clarifiers and coagulants. H. M. Spencer (Chem. Age, Jan. 1924) uses a colloidal solution of aluminum hydroxide, which on dilution forms a gel.

In the *activated sludge process* it has long been known that the effective acidity of the sewage controls proper settling, and modern methods of  $p_H$  control aid in fixing the isoelectric point, most favorable to flocculation.

Filtration through sand, coke, and the like serves to adsorb colloidal impurities, but filters of this kind do not begin to function properly until they become coated with a gel-like slime containing many bacteria. There has been much discussion as to whether the action of the filter depends on activity of the bacteria in destroying and dispersing to the crystalloidal state the finely suspended or colloidal matter, or whether the removal of these substances is not an adsorption phenomenon due to the extended surface of the filter bed. Both effects exist, the latter being the more important, and depending largely on the action of the bacterial jelly that forms the surface layer.

### Photography

The ordinary precipitate of silver bromide obtained by mixing equivalent amounts of potassium bromide and silver nitrate is flocculent and quickly settles. If the fresh precipitate (before or after washing) is shaken with a solution of gelatin containing a trace of potassium bromide, or better, yet, if the precipitate is originally formed in the presence of gelatin, there results a colloidal solution of silver bromide, which may be exceedingly fine or grainless, depending on conditions. The latter method is used mainly in preparing photographic "emulsions."



The Lippmann "grainless" emulsion is an illustration of the principle of *plural protection* discovered by J. Alexander [J. Chem. Ind. Eng. 15, 283 (1923)], for in preparing it gelatin is added to both the silver nitrate and the bromide solutions before they are mixed (see p. 43).

As a very fine emulsion is relatively insensitive, it is "ripened" by allowing the silver bromide grains to grow until they are about 0.4 to 10 microns in diameter, the process being facilitated by heat. Certain percentages of chloride and iodide may be used, a small excess of the soluble halide salt aiding in peptizing or stabilizing the precipitate, and keeping its particles within the desired limits which are about 2 to 3 microns in most cases.\*

When a sensitive ripened emulsion is exposed to light, some of the silver halide is decomposed, its halogen being probably held by the gelatin,† while the metallic silver forms a colloidal dispersion in the rest of the silver halide, yielding the so-called "photo-halides." These were long supposed to be subhalides (sub-bromide and so on) of silver, but are now recognized as being of the same nature as the "metal fogs" which often appear during the electrolysis of molten salts, and consist of colloiddally dispersed metal.

The particles of silver in the "latent image" are so exceedingly fine that, in time, they apparently recom-

\* According to Lottermoser the excess of soluble halide gives the particles of silver halide a positive charge, essential to their sensitivity to light.

† Chlorine, bromine and iodine all "tan gelatin"; see Allen's Commercial Organic Analysis, 4th ed., vol. 8, article on Albuminoids or Scleroproteins; also A. C. S. Monograph No. 11, "Glue and Gelatin," by J. Alexander.

bine again with the halogen, and the latent image fades away. To render it permanent, it must be treated with a "developer," a reducing agent which probably serves the twofold purpose of combining with the halogen and making the extremely fine silver grow into dense visible particles or grains.

The color of emulsions varies greatly with the size of their "grains." Fine blue emulsions are sensitive to red, and even to infra-red rays. Freshly prepared emulsions appear red to transmitted light, but on ripening the color changes to green, the particles increasing from below 0.1 micron to over 0.5 micron. The photo-halides resulting from the action of light on emulsions are also highly colored.

### Brewing

In the brewing process it is essential that the starch originally present be converted into sugars which can be fermented, or into very soluble dextrans. In fact both the albumin and the dextrin in beer must be finely enough dispersed to remain clear in solution. Many factors in the brewing process may tend to coagulate the albumin. The influence of solid surfaces is seen by changing the inner lining of the fermenting vessel. A certain wort, which showed 0.2450 per cent. of albumin when fermented in a glass or enameled vessel, showed only 0.1925 per cent. in a paraffin-lined vessel, and 0.1750 per cent. in one lined with pitch.

Old-fashioned brew-masters would never use any vessel unless it had first been treated with a decoction of malt kernels and nut leaves, or else with "fassge-läger" (barrel dregs) which acts like the so-called

“bierstein,” a deposit mainly of organic substances that forms on new surfaces, and prevents them from coagulating albumin.

Fluid surfaces also exercise an effect as may be seen from the fact that in the chemical analysis of beer, such substances as benzol, chloroform and benzin are used to coagulate and shake out the beer colloids.

Gas surfaces are also active. Their formation tends to coagulate the dissolved albumin, and this fact killed the so-called “vacuum fermentation process” designed to recover and use the carbon dioxide liberated on fermentation. Jarring due to transportation or passing railroad trains may have a deleterious effect. A slight trace of acid tends to stabilize the albumin, as do also the tannin and resin from the hops, the dextrins from the mash, and the inorganic colloids of calcium and magnesium. The excellent brewing qualities of the water of the River Trent (England) are in large measure due to the lime content of the water, and patents have been taken out for “Burtonizing” water by the addition of lime salts.

To secure the formation of a lasting foam and a desirable “body” (*Vollmündigkeit*), a proper balance is necessary between dextrin and albumin. Where beer is served icy cold, the chilling produces cloudiness because of the aggregation or partial coagulation of the albumin. This was cleverly overcome by Wallerstein, who introduced into the beer a proteolytic enzyme (pepsin or papain) which, by increasing the dispersion of the albumin, prevents clouding.

Isinglass and gelatin are largely used for fining beer and astringent wines. A solution of the fining agent is poured in through the bung and settles down

through the cask as a gel which effectually entraps all turbidity-producing particles. The tannin present aids in coagulating the gelatin or isinglass.

### Tanning

The skins or hides of animals consist of an organized colloidal jelly, formed of bundles of fine fibrils about one micron in diameter, bound together by cementing substance of similar chemical composition which is largely removed by liming and other treatment preceding the tannage proper. The principal protein of the hide is called collagen (*glue-former*) since from it gelatin and glue may be produced by heating with water. The old processes of bateing, drenching, puering, etc., tended to neutralize the lime and bring the collagen into a flaccid or unswollen condition; in addition, the bacterial enzymes digest off part of the remaining cementing and epidermal substances (elastin) and complete the emulsification of the fat. Synthetic mixtures consisting mainly of ammonium chloride and tryptic ferments (pancreatin) are now largely used in place of the foul-smelling bacterial baths which often ate off the grain of the skin.

Much work remains to be done to trace out the action of tanning processes and chemicals on the three colloidal elements in pelt:

1. The primary colloidal particles of the proteins.
2. The secondary colloidal particles of the proteins.
3. The fibrils of collagen (which are about  $1\ \mu$  in diameter) and other organized structures.

Tanners well know the diversity of effects that may be produced in the finished leather by varying the successive treatments before actual tanning begins; but we cannot reach a scientific understanding of the



processes at work until we separate the influence of the several factors on each of the main colloidal elements above referred to.

In vegetable tannage, the prepared hide is placed in an acid tannin solution (tan liquor), whereupon the hide powerfully adsorbs tannin and combines with it to form leather. In alkaline solution both tannin and hide are negatively charged, and no tanning occurs; in fact, leather may be stripped of tannin by alkalis. It is still a moot question whether the combination is chemical or physical, but since the fixation follows an adsorption isotherm and is very variable in percentage, it may be justly termed a colloid combination which partakes of the nature of both, but is chiefly physical rather than chemical—if we use these terms in their established meanings. The positively charged hide and the negatively charged tannin mutually coagulate each other. Neutral gelatin, if practically free from electrolytes, does not precipitate pure tannin, but in acid solution it takes a positive charge and is tanned. The tanning process may be aided by giving the hide a suitable potential, positive in the case of vegetable tannage, negative with chrome.

To prevent the skin from being “case-hardened” by too rapid a deposition of tannin, which would make it act as an ultrafilter and prevent proper tannage of the interior layers, the tanning is usually commenced in very weak or spent liquors, and the skins are moved to baths of progressively increasing strength. Non-tannins seem to play the rôle of protectors to the tannins, and the general rule is that tanning liquors having the highest tanning/non-tannin ratio are the most astringent. The degree of dis-



persion thus appears to be an important factor; for if highly dispersed, tannin easily enters the tiny interspaces between the fibrils. The efficiency of certain synthetic tanning agents used preliminary to heavy vegetable tannage may be consequent to their protective action, or their ability to enlarge the interspaces by shrinking the fibrils, thus allowing the tannin to enter the hide more rapidly and speed the tannage. [See J. Alexander, J. Am. Leather Chem. Assn., Vol. 18, p. 400, 1923.]

The degree of dispersion of the tannin and the incidental impurities present also influence the intimacy with which the tannin is fixed by the hide. By extraction with organic solvents G. Powarnin (Collegium, 1923, 222-228) obtained the following results from a quebracho tanned leather which showed a cold water extract of 9.54 per cent. by the Koch-Procter method: water-soluble material removed upon Soxhlet extraction by acetone, 12.5 per cent.; by ethyl alcohol, 17.2 per cent.; by methyl alcohol, 22.2 per cent. His tabulated results indicate that for every different tanning material used, part combines chemically and part is adsorbed.

*Chrome and alum* are believed by H. R. Procter [First Report on Colloid Chemistry, etc., British Assoc. Adv. Science, 1917] to be fixed by the hide in the form of basic salts, so that initially the tannage is largely physical. J. A. Wilson, among others, thinks that a definite chemical combination occurs subsequently. The whole process, however, seems to be a hydrolytic splitting of the salts, accompanied by adsorption (or *sorption*, to use McBain's non-committal expression), of the insoluble basic metallic salt by the

hide fiber. The increasing stability of alum-tanned leather upon aging would, then, be due to colloidal syneresis.

*Fat tannage*, which yields chamois, buckskin, washleather, and the like, is effected by introducing oxidizable oils, usually in the form of a colloidal emulsion, into the skin. The view that fat tannage is due to aldehydes, developed by oxidization of the glycerin in the fats used, seems negatived by the fact that free fatty acids themselves may serve as tanning agents. Apparently the colloidal fat and the hide, being oppositely charged, form an adsorption compound. Knapp made a fair grade of leather by simply soaking a flaccid skin in an alcoholic solution of stearic acid.

### Paper

The first paper maker was the hornet or wasp, who, by chewing up wood in the presence of his colloidal salivary secretion, imitated on a small scale the action of the "colloid mill." There is no doubt that the prolonged and thorough grinding that paper stock gets in the beater, besides bringing much of it to a swollen or gel-like state, reduces part at least to a colloidal condition. This colloidal cellulose evidently exerts a powerful cementing action, far above what would be indicated by the small percentage present by weight, resembling in this respect the "ultra-clay" which exerts so great an effect in soils. The formation of a coherent web on the fourdriner wires thus depends on the greatly extended free surface of the "stuff" or paper stock, and perhaps the addition of a little colloidal cellulose will materially shorten the time in the beater. "Onion-skin" papers are produced by excessive beating.

In *engine sizing* a colloidal emulsion of rosin in rosin soap is generally added to the beater pulp, and, after being thoroughly mixed in, is precipitated by adding alum or aluminium sulphate. The colloidal rosin and the alumina gel help bind the paper fibers together and to make the paper stronger and resistant to water. Many substitutes for rosin have been used (silicate of soda, glue, and so on) which are added in colloidal solution and subsequently precipitated. To prevent the glue from being largely lost in the back waters, some highly adsorbent filler such as talc or clay must be added to the pulp to adsorb and hold the glue.

*Tub sizing* of paper involves passing the finished web through a bath of some such colloidal solution as gelatin, glue, starch, and the like, which, on drying, fills the pores and prevents ink from spreading or "bleeding," besides adding to the finish, strength and "handle" of the paper. The nice, crisp crackle of new banknotes and of stocks and bonds is due to a bath of alum and glue.

Bibulous papers, such as *blotting paper* and *filter paper*, are made without sizing, reliance being placed for their strength on the binding properties of the colloidal cellulose. Recently rubber latex has been tried as a paper size.

The speed and the degree of drying paper are also factors materially affecting its strength.

*Colloidal clays* have found several uses in the paper industry. They tend to improve the luster of friction coated papers. Asphalts or tars may be emulsified with water by their aid, and incorporated with the paper pulp in the beater, thus serving both to size and to waterproof the paper. Old newspapers and maga-

zines may be de-inked by beating and macerating them with a little alkali and colloidal clay, which adsorbs the loosened ink so that the two may be washed away through a special screen. It is estimated that a ton of good standard newspaper can be produced from a ton and a quarter of old newspapers, and by gathering the waste in big cities alone there would be possible an annual saving equal to the cut on 275,000 acres of thickly wooded spruce forest. (Forest Products Laboratory, Madison, Wis.)

### Rubber

The milky juice (*latex*) of several kinds of plants yields on coagulation the colloidal gel called rubber. The latices are emulsions containing rubber and resin, stabilized by protective colloids (proteins or peptones) and the kind of coagulant used depends on the nature of the protector. Thus formaldehyde preserves latices whose protectors are proteins, but coagulates *kickxia* latex by precipitating the protective peptones.

*Vulcanization* consists in the combination of sulphur with rubber. The sulphur is at first adsorbed, and upon heating enters into a very close combination with the rubber, which is generally believed to be a true chemical combination.

*Fillers* increase considerably the strength and wearing power of rubber (in automobile tires, for example) by greatly extending the free internal surface. The rôle of fillers in rubber is similar to what it is in putty, and is therefore intimately bound up with their degree of dispersion. Carbon black, zinc oxide and magnesia are valued in the order given, which represents the relative order of fineness of their par-



ticles. An especially fine zinc oxide has recently been produced which is said to give the tread of automobile tires twice the life of those made with ordinary zinc oxide.

Patents have been taken out for incorporating colloidal precipitates in rubber, and even glue jelly is worked into tires to improve their wear by increasing the interior free surface.

Rubber latex is now being largely imported and used for directly impregnating fabrics which are then vulcanized, and also for adding to paper pulp in the beater. Tough, waterproof paper may be thus made.

Wm. B. Pratt has recently patented a process for dispersing commercial rubber (coagulated latex) in water (Italian Pat. 225,949, Dec. 12, 1923). Believing that the original globules in latex maintain their identity after coagulation and even after vulcanization, he incorporated protective colloids (soaps, glue) with the rubber, or formed them *in situ*, and then gradually worked in water. The rubber may first be swollen with benzol to open it up. As the coagulation of rubber was thought to be irreversible, this is practically unscrambling an egg. (See J. B. Tuttle, India Rubber World, Jan. 1924; Chem. Met. Eng., March 10, 1924.)



## CHAPTER 12

### PRACTICAL APPLICATIONS (Continued)

#### FOODS AND THEIR PREPARATION

It is a serious error to judge foods on the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate and calories alone are not fair criteria of food value; the physical condition of the food and the presence of certain "impurities" now recognized as essential (for example, vitamins) largely affect the usefulness of a food to the organism. The experience of centuries has taught us the value of cooking which hydrolyzes, swells up, or softens many foods and usually destroys the species-specificity of proteins. The Chinese sprout many grains before cooking them. "Light" bread or cake has been leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; as we learn from the Bible, unleavened bread was eaten only in times of stress. Egg-albumen, when cooked, is more slowly absorbed and its coagulum is reduced to its constituent amino-acids which are absorbed as such. Therefore, some persons who have an idiosyncrasy against raw eggs (possibly because of a permeable or ulcerated stomach wall) can eat cooked eggs.

The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter consist of tissues which age has hardened by syneresis and dehydration. In cooking meats, the exterior is seared to retain the juices (e.g. pot roast); but in cooking soup it is simmered to extract them. Many foods are highly emulsified (mayonnaise, for example), and this permits their more

ready assimilation. Cream is a natural emulsion of fat in water and *wets* blotting paper; butter is an emulsion of water in fat and *greases* paper. The presence of protective colloids in foods containing milk (ice creams, Bavarian creams and the like) is an aid to their digestibility.

The ancient art of cooking, however, involves psychological factors besides mere digestibility and ease of assimilation; taste, flavor, odor and variety are important.

From time immemorial many colloid chemical principles have been utilized in the kitchen; e.g., the making of Hollandaise sauce, mayonnaise, clarifying coffee by adding egg shells containing some adherent albumen, salting water to "set" eggs in poaching. Agar, an indigestible carbohydrate, forms a hydrous residue stimulating to the intestines.

Oysters, scallops, etc., are often allowed to "drink" fresh or brackish water, which removes repressing salts and permits swelling or plumping. In making "cream of tomato," it is usual to add some baking soda (bicarbonate) to prevent the acid fruit from coagulating the milk.

### Baking

In China, 2000 B. C., the art of baking bread was already an ancient one, and probably developed from the observation that fermentation of the dough by wild yeasts improved the bread. Bread involves a rather complicated colloidal system consisting of starch, gluten, salts, yeast enzymes, and often fat and milk. That the system must contain stabilizing factors is indicated by the fact that almost anyone, working by rule-of-thumb methods, can produce a fair loaf.

Although the temperature of a bread oven usually runs between 200 deg. and 240 deg. C., the interior of the loaf seldom goes over 95 deg. C. Wheat starch is completely gelatinized at 65 deg. C. if sufficient water be present; but as the average dough holds only about 40 per cent. of water, a large part of which is taken up by the gluten, the baked loaf is full of starch granules that have been only partially swollen and gelatinized. According to R. Whympere ("The Conditions That Govern Staleness in Bread," Maclaren & Sons, Ltd., 1919), the gluten acts as a colloidal protector to the starch, maintaining its dispersion and water-holding capacity.

The gluten of wheat flour and like grains is itself a colloidal complex and of variable composition, containing glutenin, gliadin, globulin, albumin and so on in different proportions. The baking properties of flour, that is, its ability to hold water and the leavening bubbles of carbonic acid gas evolved by the yeast, depend mainly on the physical condition of its gluten. This in turn depends on the relative ratio of the several colloids, and especially on the presence of salts which materially affect their solubility and their protective relation to each other, as is evident from the following:

Gliadin forms an opalescent colloidal solution in distilled water, from which it is precipitated by sodium chloride.

Glutenin is insoluble in water or saline solutions. It dissolves in dilute acids (or alkalis), and is thrown out again upon neutralization.

Globulin and albumin are soluble in sodium chloride solutions.

The various gluten fractions can hardly be said to be definite chemical individuals, and their purification, followed by an investigation of their mutual influence on each other, and also the influence of salts, constitutes a fruitful field for research. It is probable that we shall find here an instance of cumulative protection, where, for example, the protective action of the gliadin on the glutenin is enhanced by the protective action of the globulin and albumin on the gliadin. Salts, by changing the degree of dispersion or solubility of the several fractions, must shift the equilibrium of the complex system. So also does the slight acidity developed by the yeast. Thus, Weyland and Bischoff (Jago, "The Technology of Bread-making") found that flour moistened with a 15 per cent. solution of sodium chloride yielded a dough deficient in tenacity. Flour heated for several hours at 60 deg. C. will not make a dough, probably because one (perhaps more) of its colloids has lost so much water that the constituent particles have approached too close to be separated by water alone. This is similar to the action of gelatin, which loses its solubility upon being heated at 110 deg. C. or above.

The best results with flours are obtained by using water containing small amounts of sodium chloride. Salt, used from time immemorial, besides adding to palatability, enables the gluten to absorb and hold water, an effect shared by chlorides generally. Hard waters, containing sulphates or the like, harden the gluten; whereas, soft alkaline waters disintegrate it and destroy its elasticity. Even distilled water yields a sticky dough.

The importance of water in bread-making is obvi-



ously on a par with its importance in brewing, and in both cases the mineral impurities affect the yeast. Alum, calcium sulphate and even sulphate of copper have been used to improve gluten, especially in spoiled flours. Potassium bromate, recently introduced as a "yeast food," also registers its effect on the colloidal condition of the gluten.

While the carbon dioxide formed by the yeast is initially liberated in nearly colloidal dispersion, it soon forms visible bubbles, which, however, must be kept in fine dispersion by the elastic gluten if a loaf of good texture is expected. The addition of a little fat to the dough and the use of, say, half milk and half water, both serve not only to improve the texture of the loaf, but to add materially to its keeping properties. Whymper attributes the keeping properties of the home-made farm loaf to the protective action of fats on the starch—that is, fat tends to prevent *staling* of bread. The casein and salts of the milk also affect the gluten, and the milk fat or other added fat, by going into emulsion, tends to coat over the dough particles and prevent desiccation. Such action of the fat results in *shortening*, the resulting bread, cake or biscuit being flakier and more brittle.

### Milk

From a colloid chemical standpoint, the main constituents of milk may be classified as follows:

In crystalloid dispersion:

Salts (e.g., NaCl).

Sugar (lactose).



In colloidal dispersion:

Casein, an unstable or irreversible colloid.

Lactalbumin, a stable, reversible, protective colloid.

In suspension or emulsion: Milk fat.\*

Most formulas and recipes for modifying cows' milk for infant feeding and almost all analyses of milk combine the percentages of casein and lactalbumin under the collective title of "total proteids" (in modern form, "total protein"; globulin is also included), thereby obscuring the highly important fact that the lactalbumin stabilizes and protects the casein from coagulation by acid and rennin.

The subjoined table, giving average compositions in per cent., shows how natural milks are influenced by variations in the casein/lactalbumin ratio:

Kind of milk.	Casein.	Lactalbumin.	Protective Ratio.	Fat.	Behavior with acid and rennin.
Cow.....	3.02	0.53	0.14	3.64	Readily coagulated into large curds.
Woman .	1.03	1.26	1.13	3.78	Not readily coagulated; forms small curds.
Ass.....	0.67	1.55	2.31	1.64	

It is a striking fact that in the above table the milks are arranged in order of their digestibility by infants, which corresponds with their relative degree of colloidal protection. Thus, A. Jacobi ["The Intestinal Diseases of Infancy and Early Childhood," N. Y., 1889] stated that asses' milk has been recognized as a refuge in digestive disorders in which neither mothers' milk nor cows' milk nor mixtures were tolerated.

\* It is probable that of some the milk fat is in colloidal dispersion.

The addition of protective colloids to cows' milk stabilizes it and makes it behave like mothers' milk, when treated with acid or rennin. In modifying cows' milk for infant feeding, the usual dilution, followed by an adjustment of the fat and lactose ratios, is, of course, necessary. If enough protective colloid be added, coagulation of casein in the stomach may be entirely prevented, or, at least, the coagula kept in a very fine state of subdivision.

Besides stabilizing the casein, protective colloids have a very important effect on the milk fat, on which they exercise an emulsifying and emulsostatic influence. Indirectly their stabilization of the casein is of much greater importance, because insufficiently protected casein in curdling, entraps mechanically most of the milk fat, making a fatty, greasy curd which tends to repel the acid gastric juice and pass undissolved or only partially dissolved into the intestine, where its putrefaction causes trouble.

It is probable that the relative percentage of lactalbumin decreases with the period of lactation, so that the milk of a herd is in this respect more uniform than the milk of a single cow. With nervous women, nervous shock probably decreases the amount of albumin secreted, and this would register itself in a digestive upset in the nursling. The protective ratio of any particular mother's milk is an important factor in its usefulness to the infant.

Although their action was not perfectly understood, the most diverse kinds of protective colloids have for years been used in the modification of cows' milk for infants. For over thirty years Jacobi advocated the use of gelatin and gum arabic, and the use of cereal

gruels and dextrinized starch is familiar to all. Beer, seaweed (Irish moss) and lichens (Iceland moss) are among the protective colloids used in other lands, and in England especially, sodium citrate is much used. This protective salt, when going into solution, exhibits in the ultramicroscope actively moving ultramicros, a fact indicative of its colloidal condition.

The action of protective colloids is beautifully illustrated in the ultramicroscope, which enables us to see, in very highly diluted milk, the individual colloidal particles of casein in active motion, and to watch the course of their coagulation by acid or rennin. The casein ultramicros of cows' milk first form groups of two or three, whose motion is somewhat hampered, and they continue to aggregate into larger and still larger groups whose motion decreases as their size increases, until they finally sink out of solution in coagulated masses. If, however, some gelatin or gum arabic solution be added to the diluted milk before the addition of the acid or rennin, the casein particles continue their active "dance" and do not coagulate. In this connection it is interesting to note that the casein particles of mothers' milk appear to be much smaller than those of cows' milk, probably because of the more highly protective medium in which they are formed and exist. [See J. Alexander, *Kolloid-Zeit.* 1909, 1910; *J. Am. Chem. Soc.* 1910, 28, 280; Alexander and Bullock, *Arch. Pediat.* 1910; *J. Am. Med. Assoc.* 1910.]

Since E. Zunz showed that certain albumoses exerted a coagulative rather than a protective action, J. Alexander digested lactalbumin with rennin or rennet, and found that the resulting digestion products no longer acted as protectors in forming and stabilizing

colloidal precipitates (for example,  $\text{AgCl}$ ), but actually tended to act as coagulators. He therefore advanced the following simple colloid-chemical explanation of the rennin coagulation of milk [8th Int. Cong. Appl. Chem. 6, 12-14 (1912)]: (1) The enzyme rennin digests the lactalbumin, thereby destroying its protective action; (2) the resulting albumoses are probably coagulators; (3) calcium salts liberated from their adsorption by the lactalbumin and the like also aid in the coagulation.

When cream, or milk, heated to 50 to 60 deg. C. is forced through tiny orifices under great pressures (the pressures used are 200 atmospheres and more, and the fluid is usually spattered against an agate plate), the fat globules are much more finely dispersed, being reduced to about one hundredth their former diameter. As a consequence of the enormous increase in the free or specific surface of the system, the viscosity of such *homogenized milk* is greatly increased. The finely divided fat adsorbs so much lactalbumin (Wiegner estimates that it adsorbs about 25 per cent., as against about 2 percent. in ordinary milk), and is so highly stabilized thereby, that homogenized milk will not yield butter on churning, nor does homogenized cream churn or whip. On the other hand, because of its viscosity, homogenized cream with 17 per cent. butter fat will make as well-bodied an ice cream as an ordinary 25 per cent. cream. In fact cream is now largely kept in cold storage in the form of sweet butter, which is homogenized with sweet milk in the busy season, yielding cream again.

In *whipped cream* coagulation of the lactalbumin may be a factor too, and with Charlotte Russe and Bavarian creams gelatin is added.



Artificial milks are made by emulsifying vegetable fats or oils with protective colloids or with skim milk. Most of them are deficient in fat-soluble vitamine A.

### Ice Cream

One of the essentials in ice cream is that when it is served it shall have a smooth, mellow, velvety texture, and it is a fact amply proved by the experience of practical ice cream manufacturers and housewives, and backed by the authority of even very old cook books and recipes, that ice cream made without the addition of eggs, gelatin, or some similar protective colloid, is gritty, grainy, or sandy, or else soon becomes so on standing. The original standard for ice cream, promulgated under the Food and Drugs act, took no note of these facts, and fell when they were brought out in court during an attempt to justify this standard.

The added protective colloid tends to inhibit the crystallization of the water with the formation of sharp spicules of ice. Furthermore, it also stabilizes the casein, a matter of the highest importance; for as ice cream always contains considerably more fat than milk, the curds formed by unprotected casein would be particularly greasy and hard to digest.

A very misleading impression has been given by some food officials referring to gelatin in ice cream as a "filler," which naturally leads to the idea that it is an inferior ingredient added in quantity to cheapen the product. But as gelatin is expensive and as only about 0.5 per cent. is used, such a view is erroneous. The food value of gelatin as a protector of the body's nitrogen being generally admitted, and its effect being very beneficial from a digestive point of view, its use in ice cream is necessary, legitimate and scientific.



### Confectionery

Originally "gum drops" were made with gum arabic as a protective colloid to prevent the crystallization of the sugar and give the candy a smooth agreeable body. For cheaper grades glucose and soluble starches are now used; for, although the soluble starch is not a powerful protector, it is inexpensive, considerable can be used, and commercial glucose has but slight tendency to crystallize as about half of its dry weight consists of a highly dispersed and protective dextrin. Glucose containing too much dextrose crystallizes on standing.

"Marshmallows" are usually made with gelatin as the emulsifying, body-forming, protective colloid, but albumen and gum are also used.

In molding candies a super-dried starch is used containing only a few per cent. of moisture. Its powerful attraction for moisture tends to keep the candy in shape. Our ordinary fruit jellies and jams contain protective colloids such as pectin, which not only give body, but usually prevent the crystallization of the large quantity of sugar present.

### Gelatin and Glue

When bones, hide, or skins are heated with water, especially after a preliminary treatment in lime water followed by thorough washing, there is formed a solution that gelatinizes when cold. If the raw material is carefully selected and treated, it yields when dried a light colored transparent gelatin; if made without the precautions that should surround a food product, the result is glue.

Since the gelatins from different sources vary con-

siderably in the percentages of amino-acids they yield on hydrolysis, it seems obvious that gelatin is not a definite chemical entity, but is rather an adsorption complex whose structure is at least duplex and is probably even more complicated. The various constituents of the gelatin bear a cumulative protective relation to each other (see p. 46).

Gelatin exhibits its minimum degree of swelling at its iso-electric point, about pH 4.7, and a maximum of swelling at about pH 3, after which more acid causes contraction again. J. Loeb has explained this and many other phenomena exhibited by gelatin on the basis of the Donnan theory of membrane equilibrium, assuming that the gelatin forms salts having a non-diffusible ion (see "Proteins and the Theory of Colloidal Behavior," 1922). The facts are just as well explainable on the basis of a kinetically balanced adsorption, and in view of the variable composition of gelatin, it seems idle to speak of definite salts like "gelatin chloride" or "sodium gelatinatate." The presence of small amounts of adsorbed impurities, tenaciously held, exercises a marked effect. For this reason the so-called "water absorption test" for gelatin and glue is uncertain.

Generally speaking, the binding strength of a gelatin or glue is measured by its relative jelly strength and the viscosity shown by its solution; but the variations in these two factors do not always parallel each other. Heating causes a breakdown of the gelatin into smaller complexes; this lowers viscosity, jelly strength, and binding power, indicative of a drop from the zone of optimum colloidal stability. On the other hand, as glue solutions cool and the colloid begins to

form large aggregates, the adhesiveness also falls off (see p. 17). In choosing a glue or a gelatin for any specific purpose, *all* of its qualities and attributes must be taken into consideration, for foam, grease, color, odor, etc., may be of crucial importance (for further details see Am. Chem. Soc. Monograph "Glue and Gelatin," by J. Alexander).

## CHAPTER 13

### PRACTICAL APPLICATIONS (Continued)

#### GLASSES

While glasses consist of mixtures of silicates containing dissolved or finely dispersed impurities or additions, and while individual silicates may be isolated from glass, the constitution of the glass as a whole is not quite so simple as might be assumed from paper formulas. For it is the physical properties of glass that are the most important, and while these naturally change as the ingredients vary in kind and proportion, still the properties of parts of one and the same batch may differ widely if they are subjected to different heat treatment. Thus *Prince Rupert drops*, made by dropping part of a fluid batch of opal glass into water so that the surface was quickly chilled from 1200 deg. C. down to 20 deg. C., were clear at the exterior, becoming progressively more opalescent toward the center. Slowly cooled drops of the same batch were quite opaque throughout.

The composition of glass is so chosen that the several silicates mutually interfere with each other's crystallization (*cumulative protection*), the result being a colloidal mass in which the tendency toward crystallization may register itself by *devitrification*, a formation of relatively large crystals which render the glass turbid and injure its usual working properties. While many silicates may be cooled quite slowly without crystallizing, the silicates of calcium, magnesium, and aluminum form crystals if not quickly chilled, which is rather difficult to do because silicates in general have high thermal capacity but low radiating capacity.

Tammann (*Zeit. Elektrochem.* 1904, 10, 502) has pointed out three main factors controlling the behavior of supercooled melts: (1) The specific crystallization capacity (measured by the number of crystallization centers formed in per unit mass per unit time); (2) the speed of crystallization; (3) the variation in viscosity. To these must be added a fourth; mutual or cumulative protection.

Every substance in forming macroscopic crystals must of necessity pass through the colloidal zone, in which surface forces (adsorption, surface tension) exercise a controlling, if transient, influence that may be made permanent if sudden cooling increases the viscosity sufficiently. The adsorption of the various silicates by each other as they reach colloidal dimensions introduces a time-lag which becomes cumulative as the several silicates protect each other, and greater as the viscosity increases. Batches of glass are so mixed as to make this time-lag ample to prevent crystallization at the temperatures and during the times of melting, casting, molding and so on. When glass is cooled from the plastic to the rigid state, as in blowing, drawing, casting, etc., and especially when optical glass is being slowly cooled in melting pots, devitrification may occur through the separation of spherulites or minute crystals finely dispersed throughout the glass. The spherulitic form is usually indicative of crystallization in the presence of a colloid, and the fact that the crystals are by microscopic examination usually found to be tridymite and cristobalite points to the probability that some of the silica dissolves colloiddally in the molten silicates. Sulphates, chlorides, an excess of arsenic, and sometimes



fluorine, facilitate devitrification, thus exercising a "salting-out" action.

Practically all transparent colored glasses owe their color to the presence of colloiddally dispersed substances, usually metals or their oxides. The gold ruby glasses were carefully investigated by Zsigmondy ["Colloids and the Ultramicroscope" (trans. by J. Alexander), J. Wiley & Sons Co.]. When gold is added to a batch of glass (usually 0.03 to 0.01 per cent. of gold chloride), the melt is colorless and may even remain so on slow cooling unless the batch is regulated to prevent this. All batches, however, if quickly chilled, are colorless and optically clear in the ultramicroscope. The color is developed by reheating the colorless glass to the softening point, whereby the dissolved or crystalloidally dispersed gold begins to separate out upon nuclei ("crystallogens") already formed in the colorless glass.

If the composition and heat treatment of the batch has been such as to yield a large number of small nuclei, the color developed is a bright ruby red; for although each of these amicroscopic particles grows to colloidal dimensions, the available gold is used up before any of them become big enough to render the glass turbid. On the other hand, if a small number of larger nuclei be present in the colorless ruby glass, development leads to a dirty blue or turbid maroon shade because the dissolved gold is deposited in fewer and larger masses.

The subjoined table shows the results of Zsigmondy's ultramicroscopic examination of good and of spoiled ruby glass. Both specimens had been cooled slowly and reheated more rapidly until one

began to melt (hot end) while the other end remained cold (cold end). The fact that the average distance between ultramicros remained constant in all parts of the specimens proves that reheating formed no new nuclei.

Hot End	GOOD RUBY GLASS		SPOILED RUBY GLASS
<div style="border: 1px solid black; padding: 5px; display: inline-block;">           a  b  b'  c  d         </div>	Color Red Decreasing ↓	↓    ↓	Color blue. Ultramicros fewer, copper-red, further apart.
			Color violet. Ultramicros yellow.
			Color bright red. Ultramicros green.
			Colorless. Few faint specks visible.
Cold End			

H. F. Bellamy's results (J. Am. Ceramic Soc. 1920) show that the stannic oxide used in gold ruby glass acts as a protector to the gold, keeping the color true and deepening it so that less gold can be used. This recalls the work of Zsigmondy, who, by mixing the hydrosols of gold and stannic acid, synthesized the purple of Cassius (an ammonia-soluble deep red precipitate obtained by mixing solutions of auric chloride and stannous chloride), which Berzelius had regarded as a chemical combination of the tin sesquioxide with purplish oxide of gold.

### Metals and Alloys

Coarsely crystalline metals are brittle, because they tend to split along the lines of crystal cleavage, and

therefore the metallurgist usually aims to produce a fine-grained structure. Among the physical methods used to achieve this end are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel), and the addition of desirable constituents (carbon in case hardening, various metals in alloy steels). Thus Pütz found that the predominant effect of vanadium in steel is to decrease the size of the ferrite grains, and make the pearlitic structure fine-grained and homogeneous, yielding a harder steel.

The chief cause of fine-grained structure seems to be the inhibition of crystallization by substances colloiddally dispersed in the metal. These may be other metals, such as chromium, nickel or tungsten (or their compounds) in alloy steels, compounds such as  $\text{Fe}_3\text{C}$  in ordinary steel, or even the metal itself in the case of pure metals. The last-mentioned phenomenon is consequent on *iso-colloidism* (a colloidal dispersion of the metal in itself as dispersing phase), which may lead to *auto-protection*, the colloidal phase tending to interfere with the crystallization of the rest. Several organic compounds exhibit a similar phenomenon, yielding amorphous gels which gradually become visibly crystalline (see p. 45). It must be remembered that size alone is the criterion of the colloidal condition. As Scherrer has shown with the X-ray spectrometer, the ultramicros and even the amicros in colloidal gold hydrosols consist of tiny crystalline groups; colloidal silicic and stannic acids showed both crystalline and random or haphazard molecular clusters, while gelatin was entirely amorphous.

These experiments give us an inkling as to what

occurs during the "heat treatment" and tempering of metals, and it is to be hoped that some technique may be devised that will give us even a clearer insight than does "etching" into the changes that occur in metals in metallurgical operations (heat treatment), use, age, and even "disease" of tin for example.

With metals the crystallization forces are so powerful and act so rapidly, that a coarsely crystalline structure usually results on ordinary slow cooling. To preserve the fine colloidal structure, even in the presence of protectors, drastic chilling or quenching is often necessary.

### The Time Factor

A fact of general importance in nature, having especial application to the phenomena met with in metals and alloys, is that many transformations occur so rapidly as to elude our observation, and compel us to draw upon our imagination to follow what happens between the initial point and the end-point.\* By photographs taken thousandths of a second apart, Rayleigh showed the curious differences that occur when various liquids are dropped into water.

### Iron and Steel

When treated with dilute acid, drastically quenched tool steel does not separate out carbide of iron, but yields instead a complicated mixture of hydrocarbons. This shows that the  $\text{Fe}_3\text{C}$  is in such a fine state of subdivision that upon its decomposition the nascent hy-

\* T. W. Richards [*Am. Chem. J.*, 26, 61 (1901)] followed microscopically by instantaneous photography, the separation of crystals from solutions, and reported that the initial growth is much more rapid than subsequent growth. V. Henri applied the "moving picture" camera (cinematograph) to the ultramicroscope, and E. O. Kraemer, National Research Fellow at the University of Wisconsin, is making remarkable films of ultramicroscopic happenings.



drogen and carbon are within the range of molecular attraction which is of the order of 50 millimicrons; and the  $\text{Fe}_3\text{C}$  is in colloidal state.

Such drastically quenched steel owes its great hardness to its enormous free or specific surface, but it is too brittle to be of practical use, and must therefore have its hardness drawn or reduced. This *tempering process*, as it is called, consists in reheating the steel and keeping it at certain temperatures for various times. As soon as the temperature of the steel permits, the aggregation of the  $\text{Fe}_3\text{C}$  (or cementite, as it is known), which was suspended by the previous chilling, begins anew. Metallurgists recognize the following forms of the iron-iron carbide dispersion:

Iron-Cementite Dispersions.	Nature of Dispersion.	Crystal Structures.
Austenite . . . . .	"Solid solution"?	Structureless streaks.
Hardenite . . . . .	Colloidal . . . . .	Structureless martensite.
Martensite . . . . .	Colloidal . . . . .	Generally acicular, but varies; may be very fine.
Troostite . . . . .	Coagulation begun	Rounded or wooly (globulitic).
Sorbite . . . . .	Coagulum . . . . .	Fine pearlite, not microscopically resolvable.
Pearlite . . . . .	Coagulum . . . . .	Laminated; may segregate into balls.

Hardenite is named from its intense hardness; pearlite from its pearly luster; the rest are named after the metallurgists Roberts-Austen, Martens, Troost and Sorby, respectively.

The  $\text{Fe}_3\text{C}$  in austenite is partly, if not entirely colloidal. Hardenite and martensite represent the hardest dispersions, while troostite, sorbite and pearlite represent a decreasing order of hardness. We have here a typical instance of a zone of maximum colloidality, such as is also met with in the alloy duralumin. (See J. Alexander, J. Am. Chem. Soc. 43, 434 [1921]; Mercia, Waltenberg and Scott, Bull. 150, Bureau of Standards, 1919;



Jeffries and Archer [Chem. Met. Eng. 24, 1057, 1921] call it a "critical dispersion.") Mercia and Jeffries and Archer ascribe the hardening of duralumin to the precipitation of colloidal  $\text{CuAl}_2$ , whereas the British National Physical Laboratory believe that  $\text{Mg}_2\text{Si}$  is responsible. Probably both compounds are involved, and we may have here another instance of *cumulative protection*, where a protector is itself protected.

Jeffries and Archer\* believe that this phenomenon in steel, an analogue of which occurs in the alloy duralumin, is due to the fact that the hard particles of the dispersed phase act as *keys*, preventing any motion along the cleavage or slip planes as a whole. While this mechanical comparison may appeal to engineers, the action of surface forces, together with the fineness of crystal grain which minimizes the length of the slip planes, is quite sufficient to account for the phenomena observed.

The enormous power of these surface forces is shown by the results of some experiments privately communicated to me by P. Scherrer of Zurich. He coagulated unprotected gold sols with electrolytes, and by X-ray examination found that the tiny ultramicros (which were about  $2\mu\mu$  in diameter and showed a crystalline gold space lattice) practically fused together into homogeneous crystals of larger size. Even soft substances, if finely dispersed, will produce great increase in hardness. Thus a few per cent. of oil added to whiting makes a firm putty when ground in with it. And S. U. Pickering† made an extremely stiff mass by emulsifying 99 per cent. of petroleum oil in 1 per cent. of soap water.

\* Chem. Met. Eng., 24, 1065 (1922).

† J. Chem. Soc., 91, 2002 (1902).

The size, shape, initial heating and chilling of the piece of steel, as well as the speed, temperature and time of its reheating or tempering and speed of its second chilling, are all factors controlling the nature of the final dispersion, which is also largely influenced by the chemical composition of steel itself (percentage of the  $\text{Fe}_3\text{C}$ , presence of other metals and of impurities).

As a consequence, the proper tempering of steel requires much experience in the practical control of conditions, otherwise the optimum point is either passed or not reached; and for most uses the optimum dispersion of the cementite lies within or just beyond the colloidal zone. The addition of manganese (m. p. 1225 deg. C.) to steel retards the aggregation of the cementite to such a degree that ordinary slow cooling yields martensite. Steels containing tungsten and other metals of high melting point are known as "high speed" steels because lathe tools made with this highly protected steel maintain their hardness even though brought to a low redness by the high speed of the lathe. Under such circumstances ordinary tool steel at once loses its temper, but the high speed steels are "self-tempering."

The behavior of the iron-carbon alloys is greatly influenced by the allotropic changes of iron.

After "freezing" at about 1505 deg. C., pure iron shows upon further cooling a large evolution of heat at about 900 deg. C. known as thermal arrest point ( $\text{Ar}_3$ ), and a smaller evolution of heat at about 780 deg. ( $\text{Ar}_2$ ). Above 900 deg. the iron exists in the non-magnetic or gamma form,\* and below 780 deg.

\* A new form, delta iron, is claimed by Honda to exist at higher temperatures.

in the magnetic or alpha form, which exhibits a different crystallization from gamma iron. Between these temperatures, Rosenhain believes that the iron exists in a third allotropic form, known as beta iron, which has the crystal form of alpha iron but is non-magnetic like gamma iron. Benedicks, on the other hand, believes that the evolution of heat at 780 deg. does not indicate the change of a beta allotrope into gamma iron, but represents the final disappearance of persistent gamma iron molecular groups from the metal.

These apparently conflicting views can be reconciled by regarding the iron between 900 deg. and 780 deg. C. as an *allocolloid* or *allodispersoid*, the so-called "beta" iron being an alpha-gamma adsorption compound (alpha iron dispersed in gamma iron), whose breaking up into the more completely orientated alpha iron sets free the relatively smaller amount of heat at the point  $Ar_2$ . This view accounts for the following facts: (1) Beta iron has the same crystal form as its "predominant partner," alpha iron, but is not magnetic;\* (2) gamma iron dissolves carbide, whereas beta iron and alpha iron do not; whatever gamma iron exists in the beta zone is adsorbed by or in some loose kind of combination with the dominant alpha iron, and is not free to exert its solvent action on iron carbide; (3) the increase in strength when alpha iron is transformed into beta iron; as the temperature

\* Magnetism seems to depend not on chemical composition, but rather on a peculiar regular molecular orientation. The so-called "Haeussler alloys" are magnetic, although their individual constituents are not. According to A. W. Hull [Phys. Rev., 14, 540 (1919)], magnetism depends on the distance between atoms rather than their arrangement.

goes over 780 deg. C., some gamma iron forms, and the resulting alpha-gamma adsorption compound increases the total free surface and strength of the system; (4) the fine acicular structure of beta iron; this is indicative of crystallization in the presence of a colloid.

### Steel

The preceding remarks apply to pure iron. With the introduction of carbon, we have to deal with the iron carbide  $\text{Fe}_3\text{C}$  (cementite), and the system is complicated accordingly, dislocating the thermal arrest points.

A *low-carbon steel* (containing, say, 0.2 per cent. of carbon which dissolves in the liquid iron as  $\text{Fe}_3\text{C}$ ) when freezing down to 840 deg. C. consists of an apparently homogeneous solid solution or dispersion of cementite in gamma iron. At 840 deg. C. the alpha-gamma dispersion (beta iron) forms ( $\text{Ar}_3$ ), and at 750 deg. C. the residual alpha-gamma adsorption compound decomposes into alpha iron ( $\text{Ar}_2$ ). The steel now consists of alpha iron crystals dispersed in a "solid solution" of iron carbide in gamma iron. With further cooling the quantity of alpha iron crystals increases until at a little below 700 deg. C. the remaining gamma iron-cementite solid solution is transformed into a eutectoid mixture of alpha iron (ferrite) and iron carbide (cementite) with an evolution of heat ( $\text{Ar}_1$ ).

This last transformation seems to be the breaking up of an adsorption compound between gamma iron and iron carbide, the former transforming into alpha iron and the latter being set free to form aggregations of its own. This adsorption compound carries over



some of the gamma iron through the so-called "beta" zone to the eutectoid point, where, with increasing carbon content, increasing quantities of heat are evolved. The allotropic transformation of the iron becomes practically negligible when the steel contains above about 0.5 per cent. of carbon (which, however, means about 7.5 per cent.  $\text{Fe}_3\text{C}$ ). Steel of eutectoid composition (about 0.9 per cent. Fe, equaling about 13.5 per cent.  $\text{Fe}_3\text{C}$ ) exhibits only a single thermal arrest point, at which it glows visibly. This phenomenon, known as *realcalescence*, indicates a sudden large release of energy consequent to the breakdown of the extensive metastable system gamma iron-cementite, whereby two delayed transformations occur simultaneously—the iron transforms from gamma into alpha iron (ferrite), and at the same time the released cementite aggregates. The inhibition of the allotropic iron transformation shows that in *eutectoid steel* the large percentage of  $\text{Fe}_3\text{C}$  has carried over practically all the gamma iron in metastable condition to the eutectoid point. The presence of such elements as silicon and manganese perceptibly changes the location of the eutectoid point, illustrative of the easy disturbance of colloidal systems by foreign substances.

The iron carbide (cementite) possesses considerable cohesion and attempts to aggregate against the resistance offered by the now highly viscous iron—an ideal condition for the development of a colloidal system. The cohesive power of the cementite is so great, however, that in unquenched steels it usually appears interspersed with alpha iron (ferrite), as fine plates or fibrils, yielding the finely laminated



structure known as pearlite because under proper illumination it exhibits the iridescence of mother of

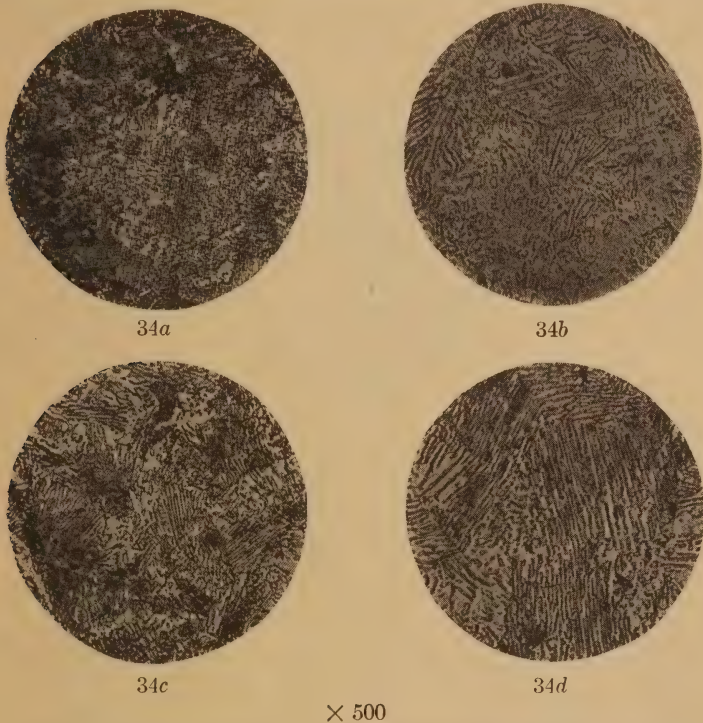


FIG. 2. MICROSTRUCTURE OF 0.85% C. STEEL, HEATED TO 800° AND COOLED AT DIFFERENT RATES. ETCHED IN 5% PICRIC ACID IN ALCOHOL.

Note how the lamellae constituting the pearlite become much thicker and more pronounced as the annealing progressed. The physical properties of the material also changed in corresponding manner.

- (a) cooled in air—largely sorbite.
- (b) cooled in lime—fine lamellar pearlite and some sorbite.
- (c) cooled in furnace—coarse lamellar pearlite showing some spheroidizing.
- (d) cooled in furnace at much slower rate than (c); the pearlite is largely spheroidized or “divorced.”

(from U. S. Bureau of Standards, Circular 113 (1922))

pearl. The iridescence is evidence of the fineness of the pearlitic structure, which, like the diatom *Pleurosigma*, taxes the highest powers of the microscope for its resolution, the lamellæ being often less than 0.2 micron apart.



43b

× 500

FIG. 3. VERY FINE MARTENSITE IN 0.46 CARBON STEEL, quenched in water after heating 15 minutes at 850° (1515° F.), just above the  $A_2$  transformation. Etched with 2% alcoholic solution of nitric acid.

Microscopically, eutectoid steel (about 0.9 per cent. C.) when slowly cooled, consists entirely of pearlite, thus corresponding to the pure eutectic of ordinary alloys.\* But with very slowly cooled steel, or with steel reheated for a long time at about 900 deg., the cementite tends to form balls or globules, the liberated ferrite at the same time forming larger crystals.

The following table shows the inter-relation of these phenomena:

\* As the Greek-derived word indicates, a eutectic is the most easily fusible mixture of two metals or other substances.

## CONDITION OF STEEL AT VARIOUS TEMPERATURES

PURE IRON	0.2 PER CENT. STEEL	0.9 PER CENT. STEEL
Gamma iron.....	Gamma iron-cementite solid solution.	This is eutectoid steel. So much cementite is present that no alpha-gamma adsorption is formed, the gamma iron being held in metastable condition by the cementite, down to Ar <sub>1</sub> .
900 deg. C. Gamma iron forms alpha-gamma adsorption compound (beta iron). Largest thermal point.	840 deg. C. Alpha-gamma compound (beta iron) forms late because of cementite.	
Allocolloidal Zone.	750 deg. C. Alpha-gamma compound (beta iron) changes to alpha iron.	
780 deg. C. Alpha-gamma compound (beta iron) decomposes into alpha iron.	700 deg. C. Gamma iron-cementite "adsorption" compound decomposes, gamma iron changes to alpha iron, and cementite is liberated and aggregates.	700 deg. C. Sudden change of all the (Ar <sub>3</sub> , 2, 1) iron from gamma to alpha, with liberation of all the cementite.
Alpha iron.	Alpha iron and cementite.	Pearlite.

The following cooling curves taken from Prof. H. C. H. Carpenter [Engineering, 107, 341, 1919] show how with growing carbon content the three thermal arrest points are combined into one in eutectoid steel:

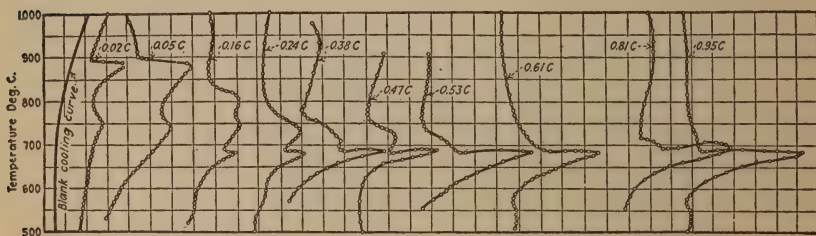


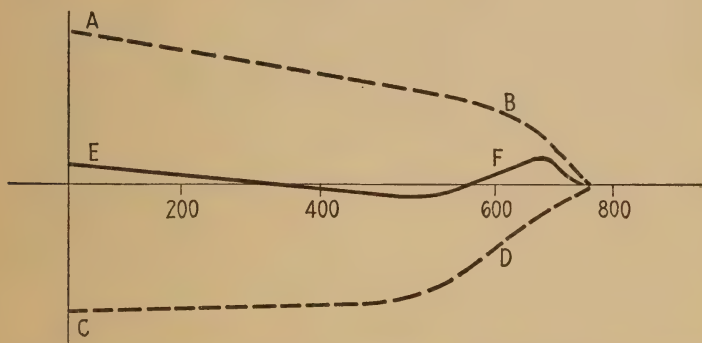
FIG. 4.—Changes in thermal arrest points of steels with increasing carbon content.

### Stepped Transformation in Steels

The aggregation of cementite takes time and there is always a time lag in the process. Consequently when carbon steel is rapidly cooled, the  $A_1$  transformation takes place at a lower temperature than when it is slowly cooled. This drop increases with the speed of chilling until it reaches about  $600^\circ\text{C}$ ., when still more drastic chilling lowers it *discontinuously* to about  $300^\circ\text{C}$ . or less.

This *stepped  $A_1$  transformation* as it is known, is beautifully explained by Kôtarô Honda who showed that it is due to the fact that in the inhibited zone the viscosity of the dispersion medium is sufficient to stop the aggregation of the cementite, but that below this zone the aggregation forces of the cementite become so powerful that they then overcome the resistance of the iron, notwithstanding the fact that its viscosity has likewise increased by cooling. The

following curve, taken from Honda's paper shows how two factors operating at various rates over a temperature range, may cause puzzling results, unless their effects can be separately analyzed.



AB = tendency curve; CD = resistance curve; EF = observed resultant.

FIG. 5.—Aggregation-viscosity curves, with resultant showing aggregation inhibited between about 600–300°.

AB is the transforming tendency or aggregating curve, plotted positively; EF is the resultant, which represents the extent to which the tendency is able to establish itself.

### Standardized Heat Treatment Terms

A committee appointed by American steel treaters has recommended the following standardization of terms regarding the heat treatment of steel. The relation of many of these terms to what has been stated above is manifest.

1. *Annealing*. Heating above the “critical temperature” followed by a relatively slow rate of cooling.

2. *Loneal*. Heating below the “critical temperature” followed by any rate of cooling.



3. *Normalizing*. Heating above the "critical temperature" followed by an intermediate rate of cooling.

Note.—In good practice the heating is considerably above the "critical temperature."

4. *Spheroidizing*. A long-time heating at or about the "critical temperature" followed by slow cooling throughout the upper part of the cooling range.

Note.—For the purpose of spheroidizing the cementite in high-carbon steels.

5. *Hardening*. Heating above the "critical temperature" followed by a relatively rapid rate of cooling.

6. *Tempering*. Reheating, after hardening, to some temperature below the "critical temperature," followed by any rate of cooling.

7. *Carburizing*. Adding carbon with or without other hardening elements, such as nitrogen, to wrought iron or steel by heating the metal below its melting point in contact with carbonaceous material.

8. *Casehardening*. Carburizing the surface portion of an object and subsequently hardening by suitable heat-treatment.

9. *Cyaniding*. A specific application of carburizing where the object, or a portion of it, is heated and brought into contact with cyanide salt.

By the term "critical temperature" is meant that temperature which is customarily associated with the following phenomena:

(a) Hardening when quenched.

(b) Loss of magnetism.

(c) Absorption of heat.

(d) Formation of solid solution.

(e) Pronounced refinement of coarse grain upon cooling.

### Tin-Lead Alloys

All mixtures of tin (m. p. 232 deg. C.) and lead (m. p. 327 deg. C.) melt below 327 deg. C.; the alloy, 63 per cent. tin and 37 per cent. lead, has the lowest melting point. If the metals are mixed in other than these eutectic proportions, the excess metal tends to crystallize out alone, having the largest possible amount of eutectic, which solidifies later. Microscopic examination shows that the eutectic is not a chemical compound; it is usually laminated and can be brought into relatively coarse dispersion by slow cooling.

But some forces do control the formation of the eutectic. As the fused alloy approaches solidification, lead, having the higher melting point, begins to form molecular groups or tiny crystals ("crystallogens"). This aggregation of lead molecules is opposed by the more fluid tin, thus lowering the freezing point of the mixture. Diminishing thermal agitation finally allows the tin to begin to form groups, and a stage is reached where both metals exist largely in colloidal state.\* In this zone a colloidal adsorption compound is formed, the ratio, 63 tin to 37 lead, being consequent on their specific forces; any excess of tin or lead is free to crystallize independently. In the eutectic, the lead by adsorption interferes with the crystallization of the tin to such an extent that, if quickly cooled, the eutectic structure is extremely fine.

As with all colloids, this represents a metastable condition, and if the temperature is kept within limits which permit molecular orientation without disruptive

\* All pure metals in solidifying pass through an isocolloidal zone, the narrowness of which is indicated by the sharp peak or cusp in the inverse-rate curve. See W. Rosenhain, "Introduction to Physical Metallurgy, pp. 85-87. D. Van Nostrand Co., N. Y., 1914.

thermal agitation, the eutectic undergoes a gradual syneresis analogous to coagulation or demulsification; a further separation into its constituent phases. The laminated structure, common in eutectics, already represents the aggregation of the preëxisting colloidal dispersion, as has been especially pointed out in the discussion of pearlite in steel.

*Solder*, used by plumbers and others, is an alloy consisting of about equal parts of tin and lead. At about 210 deg. C. it begins to extrude crystals of lead into the fluid eutectic cement, rendering it pasty and easy to "wipe," spread or mold into the desired shape. The introduction of the highly crystalline antimony (m. p. 630 deg. C.) into tin-lead alloys results in the early formation of crystals of antimony or of the hard brittle compound Sn-Sb, with the result that the ternary alloy is much harder.

*Type metal* is one of these ternary alloys whose composition varies with price and service conditions. It is usually chilled quickly, which is conducive to fine structure and hardness. White bearing metals, on the other hand, are usually cast in larger masses and chill more slowly, their composition is chosen to yield hard wear-resisting crystals of Sn-Sb embedded in a colloidal plastic eutectic, which can adapt itself to the bearing's irregularities of shape and pressure.

### Zinc-Copper Alloys (Brass)

*Brasses* containing less than 30 per cent. of zinc, irrespective of their speed of chilling, always consist of a "solid solution" of zinc in copper, known as alpha brass.

This alpha brass is really an adsorption compound between copper and zinc, in which the large

percentage of difficultly fusible copper (m. p. 1083 deg. C.) aggregates so rapidly that even in so-called "quickly cooled" specimens, the zinc (m. p. 419 deg. C.) is for the most part too finely dispersed to be much adsorbed by the copper. Hence the alloy exhibits a dendritic structure showing a copper crystallization as modified by adsorbed zinc, the amount of which increases from the center outward as the copper aggregates and the mother liquor becomes richer in zinc.\*

As Rosenhain observes, the percentage of each metal and its state of aggregation are momentarily varying during cooling, and because of the wide disparity between the melting points of the two metals, homogeneity is favored either by extremely rapid quenching from fusion (which tends to prevent the copper from aggregating) or by slow cooling and annealing, which favor the more complete dispersion and adsorption of the zinc (which is segregated by ordinary cooling).

The natural desire to introduce more of the cheaper zinc into brass is limited by the fact that with brasses containing 30 to 37 per cent. of zinc there appears a new, hard, brittle metastable phase, beta brass. Such brasses if quickly cooled are relatively hard and brittle, but if cooled slowly the beta phase disappears. With more than 37 per cent. of zinc, the beta phase is stable at all temperatures down to 470 deg. C. and the slowly cooled alloys exhibit the duplex structure found in *Muntz metal* (approximately 40 per cent. zinc). Carpenter believes that below 470 deg. C. the beta phase decomposes into alpha and gamma phases, and

\* Small pieces of alpha brass drastically quenched from fusion in liquid air will probably appear homogeneous in the microscope.



in fact that the beta phase is an almost ultramicroscopic mixture of alpha and gamma brass. (This indicates colloidal dispersion, favorable to hardness.)

Rosenhain [loc. cit., p. 145] says that the gamma brass "is exceedingly hard and brittle and its presence in the alloys renders them useless for any purpose where strength and toughness are required. This is a typical example of a law very widely applicable to alloys, viz., that those phases of a binary system which contain the two elements in anything like equal proportions are hard and brittle, only the alloys near the ends of a series being as a rule sufficiently strong and ductile to be of practical utility. We have already seen that the beta phase is harder and more brittle than the alpha, so much so that the best brasses, in which strength and ductility are of importance, are generally made with a zinc content of approximately 30 per cent., this being the cheapest alloy which does not contain the beta phase."

With solutions, as von Weimarn has shown [Kolloid-Zeit. 3, 282 (1908); *ibid.* 4, 27 (1909)], medium concentrations are favorable to the development of large crystals, whereas dilute and concentrated solutions both tend to yield colloidal dispersions; and a similar condition appears to exist with mixtures of pure metals. At both ends of the alloy series appear the larger amounts of the so-called "amorphous" phase of the metal, which in most cases is stronger at ordinary temperatures than the crystalline phase. Highly crystalline metal, deficient in the colloidal amorphous phase, is weak because it tends to split along the planes of crystal cleavage. We should therefore expect weakness where the component metals of



a binary alloy are about in equal proportions, for this concentration works against the development of colloidal metal and in favor of the larger, more perfect, but weaker crystals.

### Bronze

In their article on "Alloys"\* Roberts-Austen and Neville, in speaking of the copper-tin alloys containing less than 9 per cent. by weight of tin, say that upon quickly chilling small ingots from successively lower temperatures beginning just above the melting point, we thus learn that these alloys (bronzes) "although chemically uniform when solid, are not so when they begin to solidify, but that the liquid deposits crystals richer in copper than itself, and therefore that the residual liquid becomes richer in tin. Consequently, as the final solid is uniform, the crystals formed at first must change in composition at a later stage. We learn also that solid solutions which exist at high temperatures often break up into two materials as they cool. . . ." The work of Beilby on plastic flow and of Benedicks on quick chilling, give an insight into the behavior of metals when stressed, worked and hardened.

### Amorphous vs. Colloidal Theory

The amorphous theory of metals, advocated by Rosenhain [loc. cit., p. 249] among others, stresses particularly the entire absence of regular orientation or crystallization in the so-called "amorphous" phase, in which the molecules are supposed to be in the random, haphazard, and mainly isolated state assumed to exist in liquids. I believe, however, that

\* Encyclopedia Britannica, 11th ed., Vol. 1, p. 706.

the amorphous phase consists largely, if not entirely, of molecular groups, many of which may be oriented in the form of ultramicroscopic crystals or crystal fragments; and that its properties are due, *not to the entire lack of orientation* among its particles, but mainly to the fact that *many or most of its molecular groups are of colloidal dimensions*.

In metals the molecules are very close together and have an extremely powerful cohesion and crystallization tendency, so that it does not seem possible that the "amorphous" phase can be composed entirely of isolated atoms, molecules, or even entirely of non-crystalline groups. With the most drastically chilled metal, even allowing for the high viscosity and its rapid increase, it does not appear conceivable that no tiny ultramicroscopic crystals form, or at least that there is no grouping, regular or irregular, of the metal molecules. Even with gold hydrosols, where the dispersing water exercises a restraining influence, the X-ray spectrometer shows that both ultramicroscopic and amicroscopic gold particles are crystalline.

The facts are in harmony with the conception of amorphous metal as an isocolloid—that is, as a dispersion of colloidal crystals, crystal fragments, or non-crystalline groups, forming a solid gel-like mass. The fineness of its particles and the enormous development of free surface found in all colloids are its critical factors.\*

\* For further discussion of the colloidal state in metals and alloys see J. Alexander [Proc. Am. Inst. Min and Met. Eng., Vol. 63, 1919, and Vol. 64, 1920; Chem. Met. Eng. 1922; First Colloid Symposium Monograph, (Univ. Wisconsin) 1923]. Many of the changes that take place with sulphur are analogous to those that occur in metals. By chilling sulphur heated to 400 deg. C. in liquid air, von Weimarn [Kolloid-Zeit. 6, 250, 1910] obtained a perfectly transparent and ex-

### Electro-Deposition of Metals

The powerful effect of protective colloids on depositing metal may be readily shown by dividing a solution of lead acetate between two glasses, to one of which is added some glue solution. Upon immersing a strip of zinc in each glass, the one without the glue gives the usual bright crystalline lead "tree," whereas the other gives a very much inhibited or amorphous looking deposit. A tin "tree" shows similar results, but if some lead acetate be added to the stannous chloride solution, the lead and tin mutually interfere with each other's crystallization. In refining metals electrolytically, new very pure baths usually give coarse-grained brittle anodes, but this effect wears off as "impurities" accumulate or are intentionally added.

In other cases impurities even in minute percentage, are highly injurious. Thus one part of iron in five million may injuriously affect the quality of electro-deposited nickel. In the electro-deposition of zinc, antimony is especially troublesome, even in traces.

A large variety of *addition agents* are used, the essential being that the added substance must be adsorbed by the depositing metal when the latter is in the colloidal zone through which it must necessarily pass. Müller and Bahntje [Zeit. Elektrochem. 1906, 12, 317] found that copper deposited in the presence of colloids to keep it fine grained weighed 0.2 per cent. more than metal deposited without the colloid. They found that gelatin had the most powerful effect, exceedingly elastic sulphur. Here the rapid cooling results in the temporary preservation of a relatively large percentage of the viscous  $S_{\mu}$  dispersed in the more fluid,  $S_{\lambda}$ , the resulting allocolloid being a sulphur sulphogel or a solid sulphosol.

egg albumen considerably less, and gum and starch but little action. The relative protective efficiency of these colloids parallels their protective action in the case of colloidal gold.

An observation recently made by J. Alexander \* is of interest here. Moissan (*Comptes rend.*, 144, 593, J. S. C. I., 1907, 413) has noted that the addition of a little platinum to metallic mercury causes the latter to "emulsify" in water. Upon making up such an "emulsion," Alexander noticed that the supernatant fluid remained turbid upon standing, and therefore examined the fluid in the ultramicroscope, which revealed the presence of colloidal metallic particles in active motion.

### Boiler Scale

When water is purified before injection into the boiler, any precipitate is preferably made as coarse as possible so that it can be readily settled or filtered out. But where the precipitate is formed within the boiler, exactly the opposite result is sought. Most "boiler compounds" contain such soluble colloids as dextrin, tannin and bark extract, and some engineers put potatoes or starch in their boilers together with soda ash.

Any precipitate formed in the presence of these colloids adsorbs them and tends to remain in a finely dispersed non-coherent condition, so that it is readily removed when the boiler is blown down. The formation of hard, crystalline scale is thus prevented.

### Cement, Mortar, Plaster

Freshly mixed cement and mortar contain colloidal sols and gels which not only tend to delay or prevent

\* J. S. C. I., 1909, 28, 280.



the crystallization of dissolved substances, but also upon coagulation or setting bind the solid elements of the mixture into a coherent whole.

According to recent investigations [see A. A. Klein and A. J. Phillips, U. S. Bureau of Standards, tech. paper 43 (1914); P. H. Bates and A. A. Klein, tech. paper 78 (1916)], Portland cement contains much tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ), which is responsible for its initial set, but which alone sets rapidly into a brittle crystalline mass. However, the cement contains dicalcium silicate (possibly an adsorption compound between lime and silicic acid), like that described by Le Chatelier [La Silice et les Silicates, 1914] as being formed by adding calcium hydroxide to dilute silicic acid sol,\* which hydrates very slowly, forming an amorphous colloidal mass that evidently acts as a protector to the tricalcium aluminate, inhibiting its crystallization. Within about one day the tri-calcium aluminate begins its hydration and crystallization, which lasts about a week, and tends to make the cement weak. For the next three weeks, however, the main change is the progressive hydration of the lime-silica compound, with the development of a large amount of colloidal material which greatly increases the free surface and the strength.

The addition of such salts as calcium sulphate and the like, which are largely used in cement as a retarder, is regarded by W. Michaelis as altering the solubility of the aluminates and silicates, and by Rohland as influencing the coagulation rate of the colloids. Probably both effects co-exist, and there exists in cement a

\* From the bulky gelatinous precipitate the lime may be entirely removed by washing.



condition of cumulative colloidal protection analogous to that found in glass, flour and metals.

In the case of plaster of Paris the set may be greatly delayed by glue, gum and protective colloids, and retarders of this kind have been in use for many years. The following table shows the result of adding gelatin to plaster of Paris:

One part water contain- ing gelatin— Per cent.	Time to set in minutes.	Microscopic appearance of slide.
0	40	Characteristic crystals of calcium sulphate.
1/100	50	No crystals, except in a few spots where some colloid-free solution had diffused out.
1/10	260	No crystals.*
1/4	510	No crystals.*
1/2	960	No crystals.*
1	Not set in 48 hr.	No crystals.*
2	Not set in 48 hr.	No crystals.*

\* No regular, ordinary crystals, the mass consisting of aborted, modified or spherocrystals, or of colloidal crystals or other minute unoriented groups, or of a mixture of these.

## CHAPTER 14

### PRACTICAL APPLICATIONS (Continued)

#### CHEMICAL ANALYSIS \*

In gravimetric methods the object of the analyst is to form a non-colloidal precipitate that can be separated on a filter, washed and weighed. Von Weimarn has shown that precipitates formed in very dilute or very concentrated solutions tend to be colloidal, and for this reason the analyst usually chooses solutions of medium concentration, together with an excess of the precipitating reagent as a coagulant, acid in some cases, alkali in others. Adsorption of soluble substances by precipitates is a prolific source of error, which the analyst minimizes by thorough washing and a choice of precipitants, concentrations, and so on. The work of H. J. Weiser [J. Phys. Chem. 1919, et seq.] indicates what large errors may be due to neglect of precautions against adsorption.

Often when analytical methods speak of dissolving a precipitate, it is simply peptized or dispersed into a colloidal solution which passes through the filter paper. Thus the gel of aluminum hydroxide is readily peptized by alkali and that of iron hydroxide by hydrochloric acid.

Sometimes substances are added which inhibit precipitation by producing a colloidal non-filterable sol. Citrates and tartrates are especially apt to do this, and require special analytical treatment. The presence of such salts or of protective colloids (glue,

\* This topic has been treated at length by Prof. H. Bassett in 4th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1922.

dextrin, organic extractives) in technical products or specimens may lead to grave errors in analysis, so that the analyst should destroy them by oxidation or ignition, or else nullify their effects by a suitable excess of coagulant or precipitant. "Organic matter," as it is vaguely termed, may act: (1) By totally or partially preventing the formation of precipitates; for example, tartrates prevent the precipitation of aluminum, chromic and ferric hydroxides [Yoshimoto, J. Soc. Chem. Ind. 1908, 27, 952]; (2) by preventing the satisfactory filtration of a precipitate when formed [Mooers and Hampton, J. Am. Chem. Soc. 30, 805]; (3) by rendering precipitates difficult to wash and purify [Duclaux, J. Soc. Chem. Ind. 1906, 25, 866].

A few experiments will make this clear. Hydrochloric acid gives with lead acetate solution a heavy coagulated precipitate, but with sodium chloride, a less highly ionized precipitant, only a colloidal precipitate. If some glue solution be first added to the lead acetate, then sodium chloride produces no visible precipitate at all. In testing urine for sugar with Fehling's or Benedict's solution, as Prof. M. H. Fischer has pointed out, the simultaneous presence of albumin (or other protective colloid) is apt to bring down the copper oxide in a yellow colloidal state which, if some of the blue copper remains unreduced, appears as a greenish turbidity. For this reason the urine is boiled and filtered before testing for sugar, to separate out any albumin.

The Wassermann and precipitin tests are best understood on the basis of colloid chemistry—adsorption, peptization, protection or lack of protection, coagulation, and so on. The nomenclature of Ehrlich (com-

plement, middle-piece, end-piece, antigen, and so on), while appealing to the imagination, has no counterpart in the actual facts.

### Pharmacy and Therapeutics

The pharmacist and his predecessor, the iatrochemist, have long utilized colloid chemical processes. Mercury is readily brought into the colloidal state by trituration with fats (blue ointment) and was largely used by Paracelsus (1493–1540 [?]), though known long before. Gold was also thought to have great healing virtues, and its colloidal solutions were known. Eau-de-vie de Danzig seems to be a relic of this practice. It contains gold leaf. Thus Chaucer, in making a sly hit at the physician, says:

For gold in physic is a cordial;  
Therefore he loved gold in special.

In making emulsions the pharmacist uses gum arabic, Irish moss, tragacanth, and the like. If ferric chloride be added to gum arabic emulsion of codliver oil, it coagulates the gum, and the oil, no longer protected by the emulsostatic action of the gum, promptly separates out. Milk of magnesia may be kept in colloidal state by carbohydrate protectors.

Colloidal silver (collargol, argyrol, and the like) is an excellent germicide in many cases and a preventive of ophthalmia neonatorum. Colloidal sulphur, artificially prepared and as ichthyol (a fossil sulphur-containing fish product), is valuable in skin troubles. Colloidal mercury (hygrol, blue ointment, and the like) is largely used. The introduction of gum arabic into the normal saline solution injected intravenously in cases of bleeding and surgical shock has saved many lives. It increases and maintains the

blood pressure and viscosity. Ferric salts, especially the chloride which readily hydrolyzes into the hydrate, act as styptics by coagulating the blood colloids. Alum and antipyrine act similarly.

On the other hand, citrates, oxalates, and hirudin (extracted from the head of the leech) tend to inhibit the coagulation of blood.

### Antiseptics and Bacteriology

Colloid chemical factors largely control the action of *antiseptics*.\* To be effective a disinfectant must be adsorbed by the bacteria, and then it coagulates or peptizes their protoplasm, or else flocks them out. Natural antitoxins act similarly. Thus in the Widal test the agglutination of the typhoid germ is observed microscopically. Sodium chloride increases the effectiveness of phenol, an effect analogous to the driving-on action of salts in dyeing. Beyond a certain dose, mercury slays relentlessly. It is fixed by the kidneys and slowly causes an irreversible coagulation of the cell colloids. Lead is likewise irreversibly fixed in the body.

Dilution may remove an antiseptic before its results are irreversible.

Since bacteria are of the order of size of  $1\ \mu$ , their motion is partially Brownian, though the unequal liberation both of gas and diffusing products is also a factor. As Albert Mary has shown (*Dictionnaire de Biologie Physiciste*, 1921) the tuberculosis bacterium (Koch's bacillus) may become toxic by the selective adsorption of substances normally present in small

\* See H. Bechhold, "Colloids in Biology and Medicine," trans. by J. G. M. Bullowa; E. K. Rideal, 5th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1923. I. S. Falk, *Abstr. Bact.*, 1923.



amount in the blood (cholesterin). The extreme sensitiveness of bacteria to minute changes in acidity ( $p_H$ ) shows how intimately their life is controlled by variations in the degree of swelling or dispersion or electrical charge of their constituent colloids.

Rideal attributes the selectiveness of adsorption to the sub-microscopic inhomogeneity of the external bacterial surface, which has a checker-work of acid and basic areas. An extension of this idea justifies the now classic statement of van't Hoff that enzyme and substrate are fitted like lock and key in cases where the enzyme acts (*specific action*).

### Biology and Medicine

The changes which occur in most biological processes are remarkable, not only because of their profound nature, but also because they are produced rapidly, at comparatively low temperatures and in the presence of dilute reagents. With apparent ease the living organism disintegrates proteins, oxidizes carbohydrates and fats and synthesizes substances of great complexity. High temperatures and powerful reagents which would be destructive of life are necessary to bring about changes of this character under ordinary laboratory conditions.

### Enzymes

The high efficiency of the biological juices was once thought to be due to a mysterious "vital force," but this idea was disproved by Büchner, who isolated from yeast triturated with sand, a lifeless zymogen or enzyme which had the power of converting sugar into carbon dioxide and alcohol. Enzymes (pepsin, diastase, pancreatin, papain, lipase and the

like) are colloidal catalyzers, whose existence seems to depend on the presence of adsorbed protectors; for the more they are purified the more unstable they become. They are coagulated and inactivated by shaking, heating, electrolytes and so on, all of which cause coagulation of colloidal solutions with a decrease in their free surface and in the activity of their particles. The effective acidity ( $p_H$ ) of the solution in which an enzyme happens to be largely influences its action, probably by regulating its degree of dispersion and electric charge, which in turn affect free surface, adsorbability and kinetic activity.

Enzymes appear to act by forming with the substrate a compound of indefinite and unstable character, probably, as Sir W. M. Bayliss suggests ["The Nature of Enzyme Action"], a colloidal adsorption compound, which breaks down, liberating the enzyme again to continue the action. Croft Hill showed that the action of enzymes may be reversible, but in the organism reversion is prevented by the diffusion, dilution, or peristaltic removal of the products formed. Where increases of concentration occur in cells, tissues or organs, synthetic processes may be induced by enzymes.

Ultramicroscopically, enzymes show a multitude of colloidal particles in very rapid motion. Any substance immersed in such a solution, providing its electric charge or free fields of force permit the close approach or concentration of the enzyme at its surface by adsorptive action, must undergo a terrific bombardment, and it seems likely that enzymes produce their effects by virtue of their specific surface actions (which is influenced by the hydrogen ion concentrations of their solutions) and by the motion of their particles.

To see if this idea could be experimentally verified, J. Alexander followed ultramicroscopically the action of diastase on starch grains and the action of pepsin on coagulated egg albumen.

The diastase ultramicros, maintaining their active motion, gradually accumulated about the starch granules, which after a time showed a gnawed or ragged margin. The adsorption and motion of only the larger ultramicros could be followed, but the bright appearance of the field indicated that numerous smaller particles were present, and some of the intermediate size were seen. The albumen specimen was a dilute solution of egg white, heated nearly to boiling. It was opalescent, and showed a field full of bright, rapidly moving ultramicros which immediately clumped or coagulated into large, motionless masses upon the addition of a droplet of pepsin solution (Fairchild's containing 15 per cent. of alcohol by weight). Upon "activating" the pepsin with a droplet of decinormal hydrochloric acid, the large groups burst into small groups and isolated ultramicros, which at once resumed their active "dance." Soon, however, the albumen particles began to grow fainter and disappear, the field meanwhile becoming brighter and brighter, indicating that simultaneously smaller ultramicros or amicros were being formed. The addition of pepsin to a test tube of the opalescent albumen solution caused it to clear gradually at room temperature.

### Cytology

Physiological chemists have made illuminating researches into the chemistry of cell metabolism, and cytologists have, mainly by microscopical methods,

accumulated a wealth of interesting albeit confusing facts, the elucidation of which will lead us still nearer to an understanding of the mystery of life processes.

When a germ cell undergoes *mitosis* (or *karyokinesis* as it is also known), some of the constituents of the nucleus arrange themselves into a long irregularly twisted thread or *spireme* (loose skein), which then becomes more open but shorter (open skein). The open skein splits into short segments, frequently U-shaped, and these divide equally on either side of an equatorial plane which separates the cell into two parts, each of which develops further into a separate cell. The formation of star-like polar centers (*amphiassters*) is one of the many other associated phenomena observed.

Since the substances comprising the skein segment are readily stained by the microscopist's dyes, they are called *chromatin* substances, and the structures are called *chromosomes*. Most heritable characteristics which have been studied are transmitted solely through the chromosomes, which vary both in number and character with different plants and animals.

The problem of investigating the colloid-chemical changes underlying the microscopical picture and accompanying the chemical changes, is a most formidable one; but once it is closely envisaged, some vulnerable points will probably be found. A beginning has already been made by R. Chambers, A. Heilbronn, L. V. Heilbrunn, W. Seifriz and others. The micro-method of Freundlich and Seifriz (Zeit. phys. Chem. 104, 233-61) (which consists in pulling a tiny [ $18 \mu \pm$ ] particle of nickel through a gel by an electro-magnet of known power) shows that the



inner protoplasm of the unfertilized egg of an echinoderm (*Echinarachnius parma*) has about the viscosity of concentrated glycerin, while the peripheral layer has the consistency of a soft gelatin gel [Seifriz, *Brit. J. Expt. Biol.* 1, 431-42 (1924)].

At mid-mitosis the cytoplasm about each amphister has the consistency of a still plastic gelatin jelly, while the peripheral protoplasm of the egg becomes as viscous as bread-dough. Following the completion of mitosis, the viscosity drops again, in preparation for another division. L. V. Heilbrunn investigated the viscosity of cellular constituents by centrifugal methods [*J. Expt. Zool.* 30, 211-37 (1920)].

If in the middle of mitosis (*metaphase*) the egg be subjected to slight pressure, the whole karyokinetic spindle-shaped structure collapses, resembling in this respect (as Seifriz points out) the gel of iron oxide described by Schalek and Szegvary [*Kolloid-Z.* (1923) 32, 318-9] and that of metallic cadmium described by T. Svedberg (*Rept. Farad. Soc. and Phys. Soc. Lond. on Phys. and Chem. of Colloids*, 1921).

Some of the colloid-chemical principles involved in intercellular changes are apparently the following:

*Gel formation* (pectization)—when the gel forms in certain localities, banded orientation (Liesegang's rings) and differential diffusion may occur in it.

*Re-solution* (peptization)—this may be consequent upon the action of enzymes released or activated by changes in H-ion concentration, which may follow differential diffusion. These changes in H-ion concentration may also determine viscosity.

*Cumulative protection*—alteration of one of a connected series of protectors may produce important changes.



*Colloidal influence on crystallization tendencies*—astral rays seem indicative of this.

### Growth

The fact that structures simulating organic growths can be produced by allowing precipitates to form in colloidal gels has long been known, and many beautiful experiments may be made along these lines.\* *Differential diffusion* through semi-permeable membranes, and the resulting osmotic pressure, are large factors in growth, to which must be added the formation of insoluble chemical compounds and, especially in organisms, the manifold effects of colloidal protection, coagulation, peptization, and adsorption. Thus Wislicenus showed that the *cambial or running sap* of trees in the spring is full of colloidal substances which coagulate irreversibly after their adsorption by the wood cellulose.

The *punctum vegetationis* of plants is usually more acid than the balance of the plant (has a lower  $p_H$ ) and therefore tends to swell more and be more hydrous and tender—e.g. in the case of asparagus.

The colloidal nature of the tissues and enzymes with which food comes in contact directs and regulates the whole process of development. From the same soil we may produce a lily and a beet, a turnip and a rose. From tiny cells almost undistinguishable from each other there develop the most diverse animals; yet compressed within that space are the differences in chemical constitution and colloidal struc-

\* See R. E. Liesegang, "Kolloid-chemische Theorie des Lebens"; Stéphane Leduc, "Les Croissance Osmotique et l'Origine des Etres Vivantes"; A. L. Herrera has worked over thirty years on Plasmogeny.

ture that render possible and, in most cases, insure very tenaciously the close resemblance of offspring to parent.

Constructive and destructive processes are going on side by side in the organism, and, as R. S. Lillie puts it [Scientific Monthly, Feb., 1922], visible growth simply represents the accumulated excess of the former over the latter. Broadly, the constructive processes involve the formation of species-specific sols and gels, followed or accompanied by the formation of precipitates in their presence, and then usually by a slow syneresis which produces most of the hardenings of old age. Chemically, there is much similarity, if not sameness, about the structures formed. Thus even cartilage, the precursor of bone, is allied to chitin of insects and the mucus of snails, for all yield chondroitin-sulphuric acid. But, physically, there are enormous differences in form, percentage of composition and function.

Colloidal sols and gels exert a powerful and specific influence on developing structures, as may be seen by allowing different salts and salt mixtures to crystallize in the presence of colloids such as gelatin or gum arabic, and also by allowing precipitates to form by diffusion in various jellies (gelatin, agar and silicic acid). Although the details are of unfathomed complexity, the specificity of organisms and of the fragments, buds, spores or seeds by which they reproduce, is due to specific colloids and to the substances the colloids adsorb or whose formation they direct.\*

### Evolution

It is the general rule in biology that descendants resemble parents, and that a parent organism cannot

\* See R. S. Lillie, "Protoplasmic Action and Nervous Action," Univ. of Chicago Press, 1924.

pass on to offspring a factor which the parent did not receive from the germ-plasm of its immediate progenitors. Many apparent exceptions to this general rule have been traced to the existence in the parent gametes of recessive factors, which, while suppressed in the parent, may be liberated again in the offspring. Whether we accept the view of Darwin that large differences can represent the summation of small differences, or the more probable view of Bateson and others, that mutation or variation is a definite physiological event, no satisfactory explanation has been given as to the origin or source of these exceptions to the general rule of resemblance, although they constitute the steps by which evolution haltingly proceeds.

The crying need that we must find a chemical, physical or physico-chemical basis for mutation or variation has been voiced by many. Thus in his address before the British Association for the Advancement of Science (Australia, 1914, reprinted in *Smithsonian Report*, 1915, pp. 359-394), Sir William Bateson says: "Every theory of evolution must be such as to accord with the facts of physics and chemistry, a primary necessity to which our predecessors paid small heed. . . . Of the physics and chemistry of life we know next to nothing. Somehow the characters of living things are bound up in properties of colloids, and are largely determined by the chemical powers of enzymes, but the study of these classes of matter has only just begun. Living things are found by simple experiment to have powers undreamt of, and who knows what may be behind?"

In nature, both animate and inanimate, the following basic factors tend to produce *symmetrical orienta-*

*tion or aggregation:* (1) Crystallization and orientation in surfaces; (2) Diffusion, as in the formation of Liesegang's rings, agate, etc.; (3) Electric or magnetic fields of force; (4) Harmonious vibration as of air, water, etc. We here disregard mere chance and the conscious arrangement by man.

The main factors modifying the crystallization of pure substances are: (1) Concentration; (2) Temperature; (3) Pressure; (4) Agitation; (5) The presence of other substances, especially of colloids, which may profoundly modify crystal forms by protective action; (6) Iso-colloidism. Some substances have the power of interfering with their own crystallization, because a portion, which first reaches the colloidal state, then protects the balance.

Deviations from normal crystalline forms produced by the presence of colloids are usually symmetrical, but may not appear crystalline. Changes in the nature or degree of dispersion of the colloid, or in its percentage, mixtures of colloids, variations in salt or H-ion concentration\* of the solution, must all have an effect on the resultant quasi-crystals. Enzymes may, of course, entirely change the nature of the colloid. The species-specificity of proteins seems to be maintained by degenerating food protein to simpler forms (polypeptids and amino-acids) and then building up the specific proteins from these.

Among the factors influencing diffusion, especially in gels, are the chemical nature and particle size of the gel, and the concentration and nature of the diffusing solution. In his chapter on "Growth,

\* NaCl crystallizes in cubes from acid solutions but in octahedra from alkaline solutions.



Metamorphoses and Development," Bechhold ("Colloids in Biology and Medicine," trans. by J. G. M. Bullowa, p. 252 *et seq.*, D. Van Nostrand Co., 1920) refers to some of the remarkable diffusion figures and osmotic forms\* produced by F. E. Runge and by Stéphane Leduc, some of which resemble algæ, fungi, seaweed, etc., and even show a cellular microstructure. While pointing out the great differences between these formations and the organized structures they simulate, Bechhold says: "The physical forces which produced these inorganic formations are the same as those which produce the growth and configuration of organized material membranes, osmotic pressure, diffusion."

Perhaps the most familiar instance of modified crystallization is to be found in the delicate frost tracery on window panes, the forms being probably influenced by the glass (itself a colloid) or by substances adsorbed at its surface.† The writer has pointed out the powerful influence exerted by colloids such as gelatin, gum arabic and albumin on crystallization (Kolloid Zeit. 4, 86, 1909), and R. E. Liesegang, looking at the question from the opposite standpoint, has described the power of crystalloids to give a form to colloidal jellies (Kolloid Zeit. 7, 96, 1910). It may be said that with different salts or combinations of salts, various colloids or combinations of colloids, and variations in concentrations, temperature and speed of evaporation, will produce characteristic and generally reproducible forms on a microscope slide. A characteristic form of sodium chloride is a four-pointed star with fern-like arms which cross at a slight angle.

\* A. L. Herrera has devoted over 35 years to these studies.

† See, e.g., the figures given by Wilson J. Bentley in "Monthly Weather Rev." 1907.



A few slides made with solutions of common salts such as  $\text{NaCl}$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ , etc., containing from 0.5 to 50 per cent. of gum arabic or gelatin (figured on the basis of the dry salt), will illustrate what is meant. When a drop of the mixed solution is allowed to dry on the slide without cover glass, changes of concentration and temperature occur, giving a field that changes progressively from rim to center of the drop. A solution of one part sodium chloride, one part sodium carbonate (dry) and one tenth part gum arabic or gelatin in ten parts of water, when dried, shows in some part of the field a "flowering plant," with graceful stems and characteristic four-petaled flowers.

To see that a marked change may be produced by modifying the colloidal state of the protective substance, a slide was made with a solution containing egg albumen as the colloid. The solution was then heated until the albumen began to show a milkiness, another slide was made, and after drying was compared with the first unheated specimen. The difference in crystallization was considerable.

Unusual crystalline forms, such as sphero-crystals and sheaf-like groups which are so often seen in the crystals of substances derived from organisms, are very often consequent upon the protective action of some colloid from which they are not entirely purified. Another curious occurrence must be mentioned here, which may be termed *auto-protection* because it is due to iso-colloidism. Before reaching the ordinary visibly crystalline state, particles of every substance must pass through the colloidal zone, and the particles first reaching that state may interfere with the normal

crystallization of the rest. Thus ammonium salts, even without the addition of protective colloids, are prone to assume feathery or fern-like forms. The phenomenon is marked in the oleates and is probably the underlying cause of the formation of myelins, although their formation is fostered by such lipoid protectors as cholesterin. According to J. G. Adami (Harvey Society Lecture, 1906), if certain simple soaps be dissolved by warming on a slide with water and then allowed to cool, they may show upon examination in the polarizing microscope a perfect rain of doubly refracting spherules, which, depending on the nature of the soap, may last for hours or days or else immediately give place to a brilliant white layer of formed crystalline plates. The fluid crystals of O. Lehmann are probably examples of auto-protection, and W. B. Hardy, E. Hatschek and others have described substances which form unstable gels that soon become crystalline (see p. 45).

The bio-colloids are so readily affected by salts, H-ion concentration (effective reaction), temperature, actinic (sun's rays) and traumatic (shaking, mechanical injury) effects, that it is more surprising that plants and animals should breed true than that they should show variations. Therefore, although individuals may be much affected by such changes during their lives, it is evidently a rare occurrence that these changes are registered in the germ plasm by which alone they may be transmitted to offspring. The specificity of the germ plasm is evidently guarded by many factors, among which seem to be selective adsorption and differential diffusion of dissolved substances through its protecting walls or membranes.

Nevertheless unusual influences must occasionally change it materially without destroying it, and along this line experiment may be directed. It may be that the germ plasm can be affected through the somatoplasm, as well as by direct means. And of all the variations, in nature only the beneficial changes survive.

### Physiology and Pathology

The bio-colloids consist of carbohydrates (starch, cellulose, glycogen), proteins (albumins, globulins, ossein) and lipoids (lecithin, cholesterin, fats and oils). Each tissue has a normal state of swelling or turgor, which is greatly influenced by the effective reaction (acid if  $p_H < 7$ , alkaline if  $p_H > 7$ ) and by salts. The swelling is least at or near the isoelectric point; its increase by both acids and alkalis soon reaches a maximum, after which it falls again. Neutral salts oppose the action of acids and alkalis, apparently by driving back their ionization, and thus bringing the effective reaction (H-ion concentration,  $p_H$  value) nearer to the isoelectric point. So sensitive are colloids to minute changes in reaction detectable only potentiometrically or by the use of very delicate indicators, that fibrin will easily distinguish by a big difference in swelling, between conductivity water and ordinary distilled water, which contains  $CO_2$  and has a  $p_H$  of about 5.5.

If the *oxidation processes of the body* are normal, the hydrogen in foods is oxidized mainly to water, and the carbon mainly to carbonic acid—a gaseous acid which is exhaled without demanding protein or fixed alkali of the organism for its elimination. Nearly two pounds of caustic soda would be required to

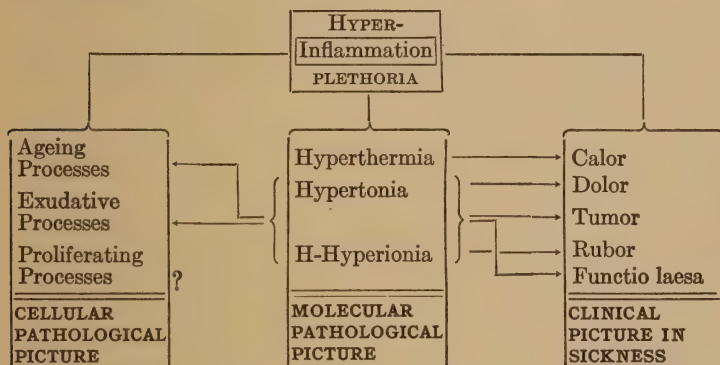
neutralize the acid produced daily by the average adult. In cases of pathological oxidation, as in diabetes, dextrose (glucose) accumulates in the blood beyond the normal average of about 1 per cent. (hyperglycemia), exerting a dehydrating or shrinking action on the tissues, while fats are oxidized only partially to the poisonous acetone, diacetic acid, and beta-oxybutyric acid, which may produce "acidosis," really a diminished alkalinity recognizable by the fact that an abnormally large quantity of sodium bicarbonate is needed to render the urine alkaline. As the body colloids are thus forced nearer to their isoelectric point, their water-holding capacity diminishes, "free" water appears in the blood, and the patient shrinks. In fact, throughout life there is a continual syneresis of the body colloids: compare the chubby hand of an infant with the shrunken hand of an old man.

Local accumulation of acid may cause swelling (*edema*); for example, insect stings which may be simulated by "stinging" gelatin with a needle dipped in acid. If acid accumulates in an organ, having a rigid capsule (eye, kidney), the swelling tends to establish a vicious circle (glaucoma, nephritis) by compressing the blood vessels and cutting down the alkaline blood stream, which is unable to absorb and wash out the acids (mainly  $\text{CO}_2$ ) formed by living protoplasm. The degeneration of the kidney in these circumstances is so typically one of the colloidal swelling and coagulation that the physician judges the condition by the microscopic appearance of the casts (hyaline or granular) sloughed off by the tubules. Certain infections (scarlet fever, for example) produce



substances likewise harmful to the kidney tissue. [See "Edema and Nephritis," by M. H. Fischer.]

The relation between the clinical, pathological, and colloid chemical pictures or complexes in inflammation has been diagrammatically illustrated by H. Schade (Münchener med. Wochenschr. 1924, No. 1, p. 1-4) as follows:



Owing to increase in quantity of dissolved substances, the osmotic hypertonia may reach as high as 11 atmospheres, while H-hyperionia may result in a hydrogen ion concentration 50 times normal.\*

### Capillary Circulation

The remarkable work of A. Krogh and his collaborators† shows that for the most part the capillaries intermittently open and close. They thus act practically as tiny railroad sidings, along which the red blood corpuscles are shoved in single file like tiny trains of freight cars. When the motion stops, oxygen diffuses slowly into the surrounding tissue served by

\* Note.—This means a  $p_H$  of between 5 and 6, which is about the acidity of ordinary distilled water not protected from  $CO_2$  absorption.

† See "The Anatomy and Physiology of Capillaries."



the capillary, while carbon dioxide diffuses about 30 times more rapidly to the red blood corpuscles. When the exchange reaches the proper balance, the capillary opens, and the arterial pressure forces the little freight cars, now loaded with carbonic acid, into the venules, their places being taken by new oxygen-containing corpuscles.

Underlying these apparently simple microscopically visible changes are many factors, chief of which seem to be the following:

(1) *Hormonal or Endocrine Control.* The posterior lobe of the pituitary yields to the blood a very potent hormone which exercises capillary control. Krogh thinks it regulates the tone of the tiny Rouget cells which embrace most capillaries; for in the frog, extirpation of this lobe causes an edema which he says is due to the relaxation of the Rouget cells. Krogh estimates that this hormone is effective in less than one part in one hundred million, while Abel has isolated a purified hormone said to be effective one part in 18,750,000,000.

(2) *Nervous Control.* There exists both a psychic nervous control ("blushing," turning pale), and a vasomotor (sub-conscious) control. Light exercises a lasting effect on the reactivity of capillaries to stimuli (work of Finsen).

(3) *Turgidity Control.* A variation in the degree of swelling or turgidity of the tissue colloids comprising the capillary wall or surrounding the capillary, would obviously result in the opening or closing of the capillary and it would seem easy to explain the process by assuming that when the tissues accumulate carbonic acid, they swell and close down on the

capillaries, relaxing again as oxygen comes in and carbonic acid diffuses out to the red blood cells. The tissues would thus automatically regulate their supply of blood in accordance with their demands; and in fact Krogh found that in exercising muscle many more and larger capillaries are open than in quiescent muscle. If anything prevents the capillary from opening again at the proper time, we have a vicious circle—an “acid” capillary surrounded by “acid” tissue—leading to congestion or inflammation.

Krogh states (loc. cit., pp. 131–133) that change in  $p_H$  (H-ion concentration) does not seem to be the dominant factor in capillary control but that this control is associated in some way with a lack of oxygen. Krogh however estimates the  $p_H$  from the  $CO_2$  tension, a method open to objections because of the many other factors which may influence the H-ion concentration of tissue, e.g. the presence of buffer salts and proteins, and selective diffusion between the plasma and corpuscles. Eliot R. Clark and Eleanor L. Clark [Anatomical Record, Vol. 27, p. 200 (1924)] found capillaries in a tadpole's tail which probably did not lack oxygen because of the thinness of the tissue, but which nevertheless automatically opened and closed, as did also segments of capillaries between Rouget cells.

It seems difficult to determine these microscopic and minute fluctuations in  $p_H$  but a technique may yet be developed. As Krogh says (p. 134), it is “a case for renewed investigation”; but it is hard to forego the belief that *variation in the swelling of tissue*, associated with fluctuation in H-ion concentration and the amount of products of metabolism, is a big factor in the control of capillary circulation.

### Psychiatry

The proper functioning of the brain and the nerves depends upon the maintenance of their constituent colloids within certain limits of swelling and dispersion. As is usual, the word *certain* is used to cloak our ignorance of the exact conditions, for the question is of great and as yet unfathomed complexity.

Broadly speaking, in most mental disorders there is a preliminary *reversible* stage, which, if not taken in time, may lead to later stages which are partially or totally *irreversible*. As the physico-chemical changes of many of the bio-colloids and proteins (e.g., gelatin and albumin when heated) show first reversible changes which gradually become irreversible as the coagulative or alterative influences persist or increase, it is natural to inquire whether incurable mental disorders may not be consequent upon irreversible changes in some of the brain colloids. When the psychiatrist says that a neurosis has become a psychosis, he is only recognizing a clinical fact without even hinting at the underlying causes.

Since the blood supply throughout the body is subject to nervous and endocrine or hormonal control (see paragraph on Capillary Circulation), and since the endocrine glands (suprarenal, pituitary, thyroid, etc.) may, by nervous stimulation and variation in their blood supply, pour their powerfully acting secretions into the blood stream, it is evident that nervous excitement or shock may affect the whole body most powerfully. Thus Crile bound a rabbit with tape so that it could not move, and allowed a tethered dog to bark at it. The rabbit died of "fright," and its brain showed extreme congestion,

probably due to the excessive blood pressure consequent upon activated secretion of adrenalin, etc., without the possibility of any corresponding motor activity to act as a natural relief valve.

Dr. A. J. Justschenko ("The Nature of Mental Diseases," Dresden, 1914) states that the viscosity of the blood is usually increased in dementia præcox, senility, and maniac-depressive insanities, especially during the periods of excitement. Auguste Lumière found that the blood of an epileptic, taken before a seizure and injected into a rabbit, produced epilepsy in the animal. The active part of the serum settled on standing and could also be centrifuged out, indicating that it is a colloidal flocculate of some sort.

### Anaphylaxis and Immunity

A. Lumière has also shown that, whereas extremely fine precipitates of inert substances (e.g., barium sulphate) are harmless when injected intravenously when freshly made, if the precipitate is aged it produces serious disturbances whose gravity depends upon the size of the flocculates. The older and more aggregated precipitates cause violent shock and death. Although the organism tends to protect itself against the formation of coarse coagula by the principle of plural colloidal protection (see p. 43), if the protective colloidal chain is attacked and broken, the formation of flocculates of injurious sizes may occur, and as these are selectively adsorbed and block the capillaries in various places, they may cause a whole train of ills, depending on the locus and the degree of action.\*

We may understand immunity as due to an antigen

\* It is believed that some bacteria (anthrax) and spirillæ (spirochete pallida) act largely by mechanically obstructing the circulation.



which has gradually, by selective adsorption, surrounded itself with a protective colloidal layer of sufficient quantity and quality that it may take up and render harmless a succeeding quantity of antigen, or else insure its agglomeration as a colloidal sol. Thus, the ultramicroscope shows that tetanus toxin and tetanus antitoxin mutually precipitate each other, as do diphtheria toxin and antitoxin. Where the absorbed protective layer is deficient in quantity or quality, we may have a hypersensitization to precipitation, so that a small succeeding dose of antigen produces a coagulation in masses sufficiently large to cause capillary embolism. In this manner we can understand the condition known as anaphylaxis and its occasional consequence, anaphylactic shock.

### Healing of Wounds

In general this process depends on the formation of a fluid exudate or transudate (sol) which later sets to a gel, cementing together the severed surfaces and, on desiccation and shrinking, forming scar tissue.

### Digestion

Crystalloids, such as sugars and salts, are diffusible through the semipermeable walls of the digestive tube, but fats and most colloidal foods must first be dispersed into a sufficiently fine state. The disintegration of proteins (meat, egg white) and of carbohydrates (starch) is effected through enzymes (pepsin, ptyalin, trypsin); while fats (either directly or after separation of their glycerin) are emulsified by the alkaline pancreatic juice. The presence of protective colloids such as mucin, cholesterin (in bile), and the like may account for some of the divergences



between the behavior of natural and artificial digestive juices. Thus, membranes moistened with cholesterol permit the passage of particles to which they would otherwise be impervious. Indeed since all body fluids contain protective colloids, no chemical action can go on in the organism without being influenced by their presence.

### Absorption, Secretion, Excretion

These are largely the results of selective adsorption by, and differential diffusion through, the colloidal tissues and fluids, accompanied by swelling and shrinking. Thus the blood is a circulating colloidal fluid which holds more water when in the "acid" or venous condition than it does when in the more alkaline or arterial condition. Tissues and organs well supplied with venous blood tend to absorb water (intestine); whereas those well supplied with arterial blood tend to give up (secrete, excrete) water (kidney). Since the blood is passing in a continuous stream, the process continues as long as the supply of water permits, or until the blood is in equilibrium with the tissues.

Conditions which decrease the capacity of the blood and tissues to hold water (diuretics, hyperglycemia and acidosis in diabetes) naturally result in the elimination of the excess or "free" water (polyuria, diarrhea).

*Minute* quantities of acid increase the swelling capacity of colloids, which quickly reaches a maximum; after which increasing acidity causes shrinking. Neutral salts oppose the action of acids apparently by driving back the ionization of the acid and thereby reducing the H-ion concentration which is a controlling factor.

The functioning of organs is largely controlled by nervous influences. Thus, a sudden nervous shock by causing vaso-dilation may send an excessive supply of arterial blood through the mesenteric arteries (in effect an "internal blush"), and cause secretion into the intestine (nervous diarrhea).

Hydrolyzable salts are readily split up upon diffusion through a colloidal gel. Thus, ferric chloride upon diffusion through agar or gelatin gel yields ferric hydroxide which is selectively held back and hydrochloric acid which differentially diffuses ahead. If a little potassium ferrocyanide and alkaline phenolphthalein be added to the colloid gel, the latter will soon be banded in patriotic red, white, and blue (see p. 49). Depending upon the structure of an organ, the location of its cavity, its arteries and veins, and its outlet, it may yield an acid secretion (gastric juice) or or an alkaline secretion (pancreatic juice). Individual substances or mixtures in the blood stream or other body fluids may be selectively separated or concentrated.

An insight into the complexity of these processes may be had by considering the functioning of the kidney. Its Malpighian tufts are plentifully supplied with arterial blood containing "free" water; but since the interior diameter (lumen) of the afferent vessels is less than that of the efferent vessels, a "back pressure" is produced which the heart-throb makes a pulsating pressure, causing the tufts to act as an ultra-filter and pour a copious but very dilute ultrafiltrate of the blood into the convoluted tubules. The tubules, however, have a plentiful supply of venous blood, which is unsaturated with water and reabsorbs most of it together with some of the substances con-

tained in the preliminary secretion; so that the concentrated excretion (urine) that finally drips into the pelvis of the kidney has in solution many substances

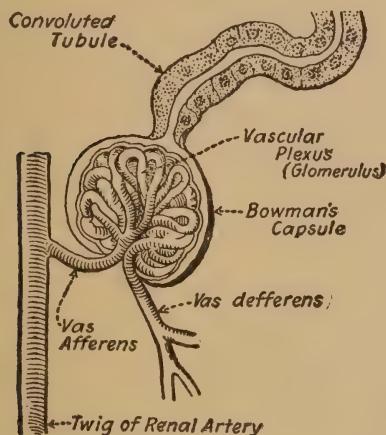


FIG. 6. Glomerular Structure.

found in the blood, but in totally different concentrations. Bechhold estimates that the average of two liters of urine voided daily by a man represents a preliminary secretion of fifty liters, forty-eight being reabsorbed within the kidney itself.

### Diagnosis

Among diagnostic methods involving colloid chemical principles may be mentioned the Wassermann, colloidal gold, colloidal mastic,\* and formol tests for syphilis, and the Widal test for typhoid. The differentiation between casts and cylindroids, usually difficult with the microscope, becomes relatively easy in the ultramicroscope or dark field. (See Alexander and Connelly, *Science*, July 27, 1923.)

\* See e.g. Adler and Sinek, *Klin. Wochschr.* 2, 2071 (1923).

### Chemo-Therapy and Colloid-Therapy

We will never understand just how many remedies work until we trace their effects on the body colloids—a most formidable task. Many remedies operative *in vivo* do not work *in vitro*.

All diseases are caused by, or involve, changes in the body colloids which, though delayed by the presence of protective substances, are sometimes irreversible. To cure the disease, we must remove the cause and aid the tissues and body fluids or “*humors*,” as they were called, to return to their normal state of dispersion and swelling. Bacteria and other invading organisms, as well as the body tissues, have highly specific adsorptive powers, and the “shot-gun” method of try, miss, and try again is our main reliance in finding something that will kill the germ or disease and spare the patient. Salvarsan was originally known as “606” because that was its number in the long series of compounds Ehrlich was testing against certain resistant organisms. Quinine, long ago known and used by South American savages, is still our specific against malaria.\* “Bayer 205,” non-operative “*in vitro*,” is said to kill the trypanosomes that cause sleeping sickness.

Many old remedies, relegated to the scrap-heap, had virtues we are beginning to understand, and they are coming into use again. Thus kaolin (clay) is largely being used as a cataplasm and internally as an adsorbent. Some varieties of clay adsorb bacteria (cholera). We laugh at Chinese or Egyptian recipes involving caterpillars, toads and the like, and even at the toad-skin ointment used by early American

\* Speke and Burton (about 1850) reported that the Congo natives attributed malaria to the mosquito and sleeping sickness. The Zulus called malaria “mosquito sickness.”



settlers, forgetting that toad-skin contains adrenalin (or an equivalent) which we accept today as one of the endocrines.

Charcoal is another colloidal adsorbent in common use; it is sometimes impregnated with drugs which it yields gradually, and it may serve as an antidote by adsorbing strychnine, for example. Freshly precipitated (colloidal) iron hydroxide was introduced by Bunsen as an antidote for arsenic; milk, egg white, and other proteins are used for corrosive sublimate poisoning; gruels or other mucilaginous drinks against aloes, cantharides, and the like. Dusting powders cool by increasing the free evaporative surface of the skin.

### Serum-Therapy

Foreign proteins (*antigens*) when introduced into the blood tend to surround themselves by adsorption with a protective film which, after a certain period, acquires in most cases the ability to adsorb, and hence nullify the effects of a subsequent dose of poison, thus conferring *active immunity*. Or the immune serum may be formed in a horse or other animal and injected (*passive immunity*). With some individuals the first doses of antigen accumulate so small a protective layer that the resulting product is *more* readily coagulated. Sensitizations of this kind may cause *anaphylaxis*, asthma, and so on (see p. 187).

### Plants

Plant tissues are likewise colloidal gels and sols, and as the sap circulates through them each tissue selectively adsorbs and elaborates certain constituents. Thus, starch-forming substances are fixed by the roots of the potato and tapioca, by the stem pith of the



sago palm and by the seeds of cereals. The stems take up the substances required for upward growth, the roots those for downward growth.

### Bio-Electric Currents

Most tissues have a potential against other tissues, the one having the higher solution pressure forming the anode.\* That solution pressure is partially dependent on degree of subdivision was shown by Hulett, and is also evident from the fact that strained and unstrained metals have a potential against each other, as do injured and uninjured tissues.

The conduction of nervous impulses (pain, sight, hearing) involves chemical changes resulting in electric currents, perhaps due to the liberation of electrons. But though we may trace the chemical or electrical effect on the brain, how this becomes *thought* or *consciousness* is still an impenetrable mystery expressed in the old philosophical circle—"What is mind?" "No matter." "What is matter?" "Never mind."

When we consider the great variety of bio-colloids and their susceptibility to change under physical and chemical stimuli with resulting changes in their behavior as adsorbents and diffusion media, we can understand why an almost infinite number of reactions may go on within their recesses, as they swing the balance of the law of mass action over particles reduced to a reactive degree of dispersion.

\* See work of R. S. Lillie.

## BIBLIOGRAPHY

---

The following are some of the more important standards of reference:

### ENGLISH

- H. BECHHOLD, "Colloids in Biology and Medicine" (trans. by Dr. J. G. M. Bullowa).  
E. F. BURTON, "The Physical Properties of Colloidal Solutions."  
M. H. FISCHER, "Edema and Nephritis." "Fats and Fatty Degeneration."  
H. N. HOLMES, Laboratory Manual of Colloid Chemistry.  
Wo. OSTWALD, "Theoretical and Applied Colloid Chemistry" (trans. by Dr. M. H. Fischer).  
Wo. OSTWALD, "An Introduction to Theoretical and Applied Chemistry" (trans. by Dr. H. M. Fischer).  
T. SVEDBERG, "Colloid Chemistry."  
WILLOWS AND HATSCHKE, "Surface Tension."  
ZSIGMONDY, "Colloids and the Ultramicroscope" (trans. by J. Alexander).  
ZSIGMONDY, "Chemistry of Colloids" (trans. by E. Spear).

### FRENCH

- COTTON ET MOUTON, "Les Ultramicroscopes et les objets Ultramicroscopiques."  
PAUL GASTOU, "L'Ultramicroscope dans le Diagnostic Clinique et les Recherches de Laboratoire."  
J. PERRIN, "L'Atome."  
A. LUMIÈRE, "L'Anaphylaxie," "Theorie colloïdale de la Biologie et de la Pathologie," "Rôle des Colloïdes chez les Etres vivantes."

### GERMAN

- ARTHUR MÜLLER, "Allgemeine Chemie der Kolloide."  
Wo. OSTWALD, "Grundriss der Kolloidchemie."  
THE SVEDBERG, "Herstellung Kolloider Lösungen."  
H. FREUNDLICH, "Kapillarchemie."  
J. VAN BEMMEL, "Die Absorption."  
R. ZSIGMONDY, German originals of above translations.

The "Zeitschrift für Chemie und Industrie der Kolloide (Kolloid-Zeitschrift)" and "Kolloidchemische Beihefte," published by Wo. Ostwald, are mines of information, containing both original articles and references.

Abstracts of, or references to, practically all current articles and books on Colloid Chemistry are to be found under the division "Physical Chemistry" of "Chemical Abstracts," published by the American Chemical Society. Furthermore, in the books above referred to, are to be found numerous valuable references.

The National Research Council has published a large Bibliography of Colloid Chemistry prepared by H. N. Holmes, and the British Association have already published five Reports on Colloids and Their Applications.

## GLOSSARY

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For the convenience of the reader, most of the less common terms employed by colloid chemists are here collected and briefly defined.

*absorption*—passage of a liquid into a solid or a gel by the action of capillarity; e.g., water by a sponge, ink by blotting paper.

*adsorption*—binding of a finely divided substance (a gas, liquid or colloidal dispersion) to an interface.

*allocolloid*—one allotrope colloiddally dispersed in another, e.g., as with sulphur.

*amicon*—a particle invisible in the ultramicroscope, usually less than about  $5\ \mu\mu$  in diameter.

*colloid*—any substance when dispersed into particles whose sizes may vary between the approximate limits  $5\ \mu\mu$  and  $100\ \mu\mu$ . The individual particles may be tiny crystals, or haphazard, random or amorphous groups; or mixtures of the two may coexist. Fineness of dispersion is the critical factor, but the effects of dispersion extend beyond the limits stated.

*deflocculation*—dispersion of aggregates or flocculates.

*emulsion*—a fine dispersion of one liquid in another. The dispersed particles may or may not be of colloidal size; if not they usually form a cream layer on standing long enough.

*emulsoid*—a colloid in which both phases are a liquid.

*gel*—an aggregation of colloidal particles into practically non-motile larger groups. Internal readjustment may cause syneresis (q.v.).

*hydrophile*—literally “water-loving”; applied to colloids which tend to remain dispersed, hold water or remain in solution (see lyophile).

*hydrophobe*—literally “water-hating”; applied to colloids which tend to aggregate and shed water, or fall out of solution (see lyophobe).

*hysteresis*—time-lag in the aggregation of colloidal particles.

*interface*—the surface between two phases.

*irreversible*—a colloidal dispersion that will not redisperse after desiccation at ordinary temperatures.

*isocolloid*—a substance colloiddally dispersed in itself, e.g., as colloidal ice in water.

*Liesegang's rings*—bands or rings usually regularly or rhythmically placed, which form when precipitates are produced by diffusion in jellies or similar structures.

*lyophile*—literally “solution-loving”; same as hydrophile, but also applicable to dispersion media other than water.

*lyophobic*—literally “solution-hating”; same as hydrophobe, but also applicable to dispersion media other than water.

*micron* ( $\mu$ )— $\frac{1}{1,000}$  mm.

*milli-micron* ( $\mu\mu$ )— $\frac{1}{1,000} \mu = \frac{1}{1,000,000}$  mm. = 10 Å.

*orientation*—disposition in space or on a surface, relative to certain points, lines or surfaces. Opposed to molecular chaos.

*pectization*—gelatinization; an aggregation of colloidal particles into masses of sufficient size to be substantially devoid of Brownian motion, the resulting mass forming a flocculent precipitate; gel, or jelly, according to conditions.

*peptization*—the reversal of pectization; the dispersion of a solid colloid by an enzyme (e.g., pepsin, whence the term) or by simple action of a dispersing agent (e.g., of  $\text{FeCl}_3$  gel by traces of  $\text{HCl}$ ,  $\text{SiO}_2$  gel by traces of  $\text{NaOH}$ ), or by heat (gelatin).

*protection*—inhibition of aggregation.

*protector*—a substance, usually a reversible colloid, which prevents or tends to prevent the aggregation of colloidal particles.

*reversible*—a reversible colloid is one that redissolves after desiccation at ordinary temperatures.

*sol*—a colloidal dispersion whose particles have sufficient Brownian motion to keep them in solution. The dispersing medium is often employed as a prefix: e.g.,

hydrosol = in water

sulphosol = “  $\text{H}_2\text{SO}_4$

alcosol = “  $\text{C}_2\text{H}_5\text{OH}$

aerosol = “ air

pyrosol = “ a melt (glass, metal, etc.).

*specific surface*—external, free, or rind surface per unit wt.

*submicron*—ultramicro.

*suspensoid*—a colloid in which the dispersed phase is a solid.

*syneresis*—aggregation of particles in a gel, with incidental liberation of liquid.

*ultrafiltration*—filtration (usually under pressure) through very close pored gels or jelly septa.

*ultramicroscope*—a compound microscope having a dark field and means of intense illumination of the object to be examined by a beam of light preferably at right angles to the optical axis of the microscope. Particles are thus seen by the light they diffract.

*ultramicro*—a sub-microscopic particle visible in an ultramicroscope.



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